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INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, November 12, 1947. Mr J. A. Oriel, C.B.E., M.C. (Vice-President) presided.

The Minutes of the preceding Ordinary General Meeting, held on October 8, 1947, were read by the General Secretary, Mr. F. H. Coe, confirmed, and signed.

The Chairman (Mr J. A. Oriel): We have asked Dr Lee, who is in charge of the Bitumen Section of the Road Research Laboratory, to take the chair at this meeting.

There is no need for me to introduce Dr Lee as most of you know him very well. I now invite him to occupy the chair.

Dr A. R. Lee, on occupying the chair, said: I appreciate the honour you have done me in asking me to occupy the chair at this meeting. You will no doubt be interested in the circumstances that have led to our meeting this evening. During a recent discussion by a Committee of this Institute I sat next to Dr Saal, and in the course of our discussions, as is always the case when we talk about bitumen, we got on to the subject of viscosity. I am not sure whether somebody asked "What is viscosity?", but we certainly asked how to measure it and the question arose "Is it possible to introduce a standard method for measuring the absolute viscosity of bitumen?" It sounds a very simple question; but we discussed it throughout the afternoon and we wound up by asking if Dr Saal could give us a paper reviewing the subject. I think that is the origin of this meeting; and perhaps for that reason I have been asked to take the chair, in the hope that I might be able to bear part of the burden.

I think everyone present knows about Dr Saal. This is the first occasion since the war that we have had the pleasure of hearing a paper by him. We had several before the war, and we always look forward to his papers, first, because of their high standard, and secondly, because of the neighbourly relations we always like to maintain with our Dutch friends.

Dr Saal then presented the following paper.

RHEOLOGICAL INVESTIGATION OF ASPHALTIC BITUMEN IN CONNEXION WITH ITS TECHNICAL APPLICATIONS.

By R. N. J. Saal.*

Introduction.

For nearly twenty years extensive investigations into the rheological properties of asphaltic bitumens and their compositions have been carried

* N.V. de Bataafsche Petroleum Maatschappij.

out. The knowledge obtained has in numerous cases given a better understanding of the function of asphaltic bitumens in their technical applications. It is felt, however, that additional information is still required and it is worth while to reconsider the following points:

(*a*) What do we know about the rheological properties of asphaltic bitumens and their compositions?

(*b*) What do we want to know and how can we obtain the information that is still lacking?

To get a general survey it is necessary to cover the whole field of the applications of asphaltic bitumen; so its use in road construction as well as its industrial applications must be included in the considerations.

Present Knowledge.

In technical applications asphaltic bitumen is chiefly present in three different forms: as such, mixed with filler (*e.g.*, with 25 per cent by vol), and as a binder in more or less graded mineral or other aggregate mixtures. Especially extensive knowledge of rheological behaviour is now available in the first and in the last case. Further, the bitumen can be present occluded in a structure of other material (impregnated materials).

Pure Bitumens.

Before investigations were started, the mechanical behaviour of asphaltic bitumen was judged from penetration, softening point, viscosity at high temperatures, and similar tests. Considering the complex rheological behaviour, following already from the prominent elastic character of most bitumens, it was evident that these kinds of investigation could never give a complete picture. Methods were needed in which the principal variables, stress and deformation time, could be applied in a simpler way.

In the beginning the investigators, who tackled this problem, chose experimental conditions under which the course of the deformation was easily observable. Deformation times from some seconds up to days and more, and shearing stresses from 10^2 to 10^6 dn/cm^2, were used in such combinations that shears with a minimum of about 0·01 up to, *e.g.*, 100 were obtained.

Several types of apparatus were used. The concentric rotation type of viscometer was especially considered as a suitable type, as substantially the same shearing stress is applied in every point of the material under investigation, while the stress can be applied for every desired time. Other types, the Pochettino viscometer, the torsion and the parallel plate plastometers as well as capillary viscometers were also used, notwithstanding the fact that a derivation of the behaviour under constant shearing stress for any desired time was not possible or more difficult in these cases.

The results of these investigations gave rise to a better understanding of the above-mentioned routine determinations, so that a deduction of the rheological type of asphaltic bitumens from such routine determinations became possible. Further, these investigations were the main basis for the derivation of the structure of the different kinds of bitumens. Last but not

least, in a number of cases a better understanding could be obtained about the relation between the behaviour of bitumen in practice and their routine analysis, *i.e.*, in such cases where the condition of stress and time in practice and in the laboratory were more or less the same.

A brief summary of these results is as follows :

(1) At ordinary temperatures bitumens show a rheological behaviour according to one of the following three types, depending upon origin and method of manufacturing :

(*a*) A viscosity practically independent of shearing stress or time;

(*b*) A viscosity being substantially independent of stress after a certain deformation, but accompanied by a distinct elastic fore- and after-effect;

(*c*) A retarded elastic deformability with appreciable permanent deformations of a thixotropic character only at high shearing stresses or long deformation times.

Further consideration in connexion with composition and colloid structure of bitumen lead to the conclusion that bitumens showing types (*a*) and (*b*) must be considered as sols, whereas the last type is shown by bitumens of a gel character. The difference between (*a*) and (*b*) is governed either by the micelle (asphaltene) content or by the elastic character of the micelles.

(2) Up to the ring-and-ball temperature the elastic deformability under the same shearing stress is little dependent upon temperature.

(3) Between normal temperature and the ring-and-ball temperature the relative change with temperature in the final rate of deformation at constant stress is little dependent upon the type of the bitumen.

(4) At high temperatures all bitumens show a viscosity practically independent of stress or time; the elastic effects can no longer be measured owing to the low viscosity at these temperatures.

(5) At low temperatures ($<15°$ C) only few investigations have been carried out. For soft bitumens the behaviour can be deduced from that of harder bitumens at higher temperatures. For hard bitumens, however, further information is still desirable.

(6) The influence of pressure upon the viscosity is very large. Whereas lubricating oils show a viscosity increase of about 25 per cent per 100 atm, bitumens show an increase of 100 per cent and in special cases even up to 250 per cent. In all these cases an exponential relation exists

$$log \frac{\eta_p}{\eta_0} = \frac{p}{p_0}$$

in which p is the pressure and p_0 a constant.

(7) The penetration determination, according to the A.S.T.M. method D5–25, is a means of evaluating the viscosity characteristics of bitumens.

For bitumens of type (*a*) there is a direct relation between penetration and viscosity; $\eta = 1{\cdot}58 \cdot 10^{10}/\text{pen}^{2{\cdot}16}$.

The relation of the penetration with varying penetration time is intimately connected with the degree of the elastic effects. In general, the following equation applies :

$$l = At^n$$

in which l is the penetration depth after time t and t duration of penetration.

The exponent n shows a value of about 0·5 for bitumen of type (*a*), of about 0·45 to 0·3 for type (*b*) and of about $<0{\cdot}3$ for type (*c*). In the range of normal temperatures n is practically independent of temperature.

These differences in n mean that bitumens showing the same penetration under standardized conditions ($t = 5$ seconds) can show different penetrations at other penetration times. Moreover, a different picture is obtained of the temperature susceptibility of a bitumen when comparing penetrations at $t = 5$ seconds at different temperatures and when comparing penetration times for the same penetration depth at these temperatures. In connexion with the slight influence of temperature upon the magnitude of the elastic deformations the last method must be considered as giving a better impression of the temperature susceptibility of the viscosity of bitumens. In accordance with (3), only small differences in temperature susceptibility of bitumens of different types are found in the last-mentioned way.

(8) The viscosity of bitumens of type (*a*) and (*b*) at the ring-and-ball softening point (A.S.T.M. method D36–26; E28–42T) is about 1 to $2{\cdot}10^4$ poises.

During the last few years a new trend has been perceptible in the rheological investigation of asphaltic bitumens and their compositions, *i.e.*, by means of the measurement of the dynamic elasticity modulus and the mechanical loss during vibrations. Nor is it in this case possible to go deeply into the details of this new research tool; a few remarks may suffice.

The dynamic elasticity modulus bears no direct relation to the elastic fore- or after-effect mentioned previously. Bitumens of class (*a*), for example, show no elastic fore- and after-effects (later described by static elastic effects); in vibration, however, they behave like solid materials and show an elasticity modulus of about 10^{10} dn/cm^2 (room temperature). Whereas the static elastic effects must be considered as closely related to the elastic properties of the micelles of the system, the dynamic effects depend on the properties of the total system.

The mechanical loss, which can be expressed by means of an angle of loss in the same way as in the electrical analogy, is of the same order of magnitude or larger than that of rubber. Figures for $tg\,\delta$ of about 0·1 to 0·5 are generally found. This means that mechanical vibrations in bitumens are strongly damped.

This mechanical loss must be closely connected with the viscosity characteristics of the system. A curious fact, however, is that, while one may expect a proportionality between loss and frequency, in the same way as in the electrical analogy, the experimental facts point to an almost constant loss. An explanation of this phenomenon, which is also found with other materials, still gives great difficulties. This means, that at the present no direct relation between the dynamic and the static viscosity characteristics can be given. To obtain an insight into the behaviour of bitumen during very rapid deformations an extrapolation from measurements about slow deformations, is, therefore, not yet feasible.

Summing up, it can be said that extensive information especially about the softer bitumens is available about the rheological behaviour of bitumens

at temperatures between room temperature and ring-and-ball temperatures and at shearing stresses from about 10^2 to 10^6 dn/cm^2 for deformation times above some seconds. However, our knowledge about the dynamic behaviour is still very limited.

Bitumen-filler Mixtures.

Investigations into the rheological properties of bitumen-filler mixtures have been made by means of determinations of the penetration and the ring-and-ball softening point of series of mixtures with increasing filler content. It has been found that for a number of fillers the volume of filler present particularly determines the properties of the mixture. However, in a number of cases, other properties of the filler are of predominant importance, *e.g.*, in the case of long-shaped particles, porous structures, etc.

When measuring the viscosity characteristics of bitumen filler mixtures in a more theoretical way, it is found that dilute mixtures of bitumen of the most simple viscosity characteristics (class (*a*)) with fillers of the first group show a viscosity according to Einstein's law, which states that 1 per cent by vol of solid material increases the viscosity by 2·5 per cent. At somewhat higher concentrations (*e.g.*, 10 to 20 per cent by vol) the increase in viscosity is larger. Here, too, this increase is in accordance with the behaviour of other kinds of systems, for which the general empirical relation given in Table I applies.

TABLE I.

Relative Viscosity of Suspensions.

% by vol.	Relative viscosity.
10	1·3
20	1·9
30	2·8

No influence of shearing stress on viscosity has been found in these dilute suspensions.

At still higher concentration of filler in bitumen the viscosity becomes dependent upon the shearing stress, and a yield stress may be found. These deviations can be explained by assuming that a kind of skeleton between the particles is formed. Little is known about this phenomenon, at least from direct measurements upon such mixtures.

It is to be expected that the elastic fore- and after-effect of the bitumen of other groups will give rise to similar effects in mixtures with filler; information about this point is, however, very scarce. Further, it is to be expected that fillers of long-shaped form can give the same effect; here, too, our knowledge is very limited.

As far as the dilute suspensions are concerned, the influence of temperature and pressure upon viscosity is the same as that for the bitumen itself. In the more concentrated mixtures, where deviations from simple behaviour occur, the influence of temperature must become more complicated, as changes in coherence between the particles must occur. Here, too, our information is still very limited.

The same applies to mixtures with fillers of fibrous or laminar form. A more or less quantitative relation between the shape of the particles and the viscosity increase cannot be given.

Lastly, it may be remarked that the dynamic behaviour of bitumen-filler mixtures must be closely connected with that of the bitumen. Here, too, investigations are desirable.

Summarising, it can be said that the knowledge of the rheological behaviour of bitumen-filler mixtures is still very incomplete. This must form a serious drawback for the understanding of the properties of the next step in bituminous compositions, namely, mixtures of bitumen, filler, and coarser aggregate.

Bitumen Mixed with Graded Aggregate.

Mechanical investigation of mixtures of bitumen with graded mineral aggregate (consisting of filler and coarser material), especially in connexion with their behaviour as road-building materials has already been carried out for a long time. Generally the methods applied were copied from the methods used for elastic solid materials (especially cement). In this way a thorough investigation into the plastic properties of these mixtures could not be carried out.

Furthermore, the special composition of these mixtures introduces a new variable, as compared with ordinary plastic materials, namely, the great influence of an omnilateral pressure upon the resistance against deformation. The mixture, being composed of loose particles, when containing a certain amount of voids, will give rise to a considerable friction between these particles when subjected to pressure, in the same way as is found in soil mechanics.

For a better understanding of the mechanical properties of such mixtures, a method must be used in which a homogenous state of stress is present in the material (just as was necessary for pure bitumen). Furthermore, the method must give the possibility of studying the influence of an omnilateral pressure upon the friction between the coarser particles.

Nijboer developed such a method for the investigation of the plastic properties of such mixtures. Previously, Hveem introduced an analogous method without studying, however, the influence of the rate of deformation. From Nijboer's work it can be concluded that the resistance against deformation of bitumen-aggregate mixtures can be divided into three parts:

(1) a frictional part, resulting from the mutual friction of the aggregate particles under influence of the omnilateral pressure. This frictional part is only present when the mixture contains a certain amount of voids, so that compression of grain to grain is possible. It has been found that the corresponding coefficient of friction is always about 0·6, independent from the temperature and the nature of the bitumen, this property therefore does not give rise to further discussion.

(2) a part having the nature of a yield stress (initial yield stress). This part increases with the amount and fineness of filler in such a way that it must be connected with a kind of coherence between these particles in the same way as described under bitumen-filler mixtures.

The composition of the bitumen was found to have a great influence upon the magnitude of this effect, as well as the temperature.

(3) a part having the nature of a (differential) viscosity, this viscosity being dependent upon the shearing stress. The viscosity of the mix is appreciably higher than that of the bitumen component, the ratio often being of the order 10^4 and higher. The viscosity depends again upon the amount and the fineness of the filler, in this last respect the viscosity shows the same dependency as the initial yield stress, so that there are strong reasons for assuming that its origin must chiefly be sought in these points of contact of the filler particles. Here, too, the composition of the bitumen is of considerable influence.

The way in which the resistance is split up in these three parts cannot be discussed here in connexion with the available space.

Little is known about the influence of the type of the bitumen (classes (*a*), (*b*), or (*c*) mentioned before) upon the properties of the mix. However, the impression exists that this influence is not predominant.

The influence of increasing temperature consists in a decrease of the yield stress and the viscosity. However, at normal temperature the temperature susceptibility of the viscosity of the mixture is appreciably smaller than that of the bitumen component, when a comparison is made at the same rate of shear. At low temperatures the viscosity of the mixture seems to increase to an almost infinite value in a short range of temperatures, so that the introduction of a special solidification temperature for this purpose has been considered advantageous.

There is no sense in comparing the influence of the pressure upon the viscosity of bitumen and that of these mixtures, as the mechanism is quite different in these cases. In the former case, the influence is the normal one of pressure upon viscosity of liquids, whereas in the latter case the influence of pressure consists in an increase of the frictional resistance between the coarser part of the mineral aggregate.

From the foregoing it is evident that the mechanical resistance is mainly set up in the points of contact of the aggregate particles, especially those of the filler. An analysis of the phenomena during shear in these points is highly complicated. The following remarks may illustrate these difficulties :

(1) It is highly probable that adsorption phenomena occur at the interface between bitumen and aggregate, giving rise to a change in composition of the bitumen in these layers. In this case no direct relation between the rheological properties of the bitumen and those of these layers and therefore of the total mix can be expected. Adsorption can take place with the micelles of the bitumen, polar substances (in the form of naturally-occurring component or of additives).

(2) Even without such adsorption phenomena this problem is highly undetermined. The shape of the contact areas, the rate of displacement, and the load can hardly be given even in order of magnitude; therefore a calculation of the resultant resistance can only be given in a highly approximate form.

The investigation into the dynamic behaviour of mixtures of bitumen with graded aggregate is still in a state of development. Some information

exists about the dynamic modulus of elasticity, which is found to be strongly dependent upon temperature and further to be connected with the kind of bitumen. With the range of bitumen contents found in practice the modulus is almost constant, other circumstances being the same. Information about the mechanical loss during vibration is still lacking.

Summing up, the mechanical properties of these mixtures under more or less static conditions must be considered to be known to a considerable degree, so that the application of this knowledge to practical questions, especially road construction, is possible. However, the dynamical side is still in a first stage of investigation.

Desirable Knowledge and Methods of Investigation.

For a complete understanding of the mechanical behaviour of bitumens and bituminous compositions in their practical applications on the basis of the knowledge of their mechanical and especially their rheological properties, an analysis has to be made of the mechanical conditions of these applications.

Further, as far as mixtures of bitumen with other materials are used, the connexion between the mechanical conditions of the mixture and these of the bitumen component has to be considered.

Only after such an analysis can be answered the question in what circumstances the rheological behaviour of bitumen must be known.

Mechanical Conditions Affecting the Total Material.

The mechanical conditions affecting the total material and the construction can be described by the magnitude of the stresses or the rate of strain and the duration of these mechanical influences.

In a number of cases this description can be given more or less easily. This is especially the case when static conditions are present. When sufficient knowledge about the material is available, so when it is known whether viscous, plastic, or elastic behaviour has to be supposed, calculations can be made giving the state of stress in different points of the construction as a function of the load applied or of other mechanical actions upon the constructions. Total deformation of the construction and most severe conditions occurring at a certain point of the construction will be the main points of interest.

A few simple examples are:

(1) A layer of bitumen placed under a certain angle (α) with the horizontal (*e.g.*, bitumen in roofing felts) under influence of its own weight. Here, the maximum shearing stress is equal to $d\phi g \sin \alpha$ dn/cm^2, in which d = layer thickness (cm), ϕ density bitumen (gr/cm^3) g = acceleration due to gravity (cm/sec^2). Duration of application infinite. In this case shearing stresses of the order of some 10^2 dn/cm^2 are present.

According to the foregoing determination of the corresponding flow is within present experimental possibilities.

In other cases other forces can be exerted to the bituminous coat (*e.g.*, coatings on pipes buried in the ground). After having deduced

the magnitude of these forces (*e.g.*, from soil mechanics) the case can be treated in the same way.

(2) Bending of a layer of bitumen. The maximum relative elongation in this case amounts to $d/2R$, in which d = thickness of the bituminous layer and R radius of curvature, so that elongations of 10 per cent can be easily obtained. Assuming a time of bending of 1 second and a viscosity of 10^6 P, a maximum shearing stress of the order of 10^5 dn/cm^2 is developed in the material. The elastic fore-effect can be of considerable influence here.

(3) A layer of a mixture of bitumen with filler and coarser aggregate under influence of a static load (*e.g.*, a bituminous carpet under a standing car). According to calculations of Prandtl the bearing capacity of a plastic material with a certain angle of friction is the product of the initial yield stress and of a function of the angle of friction. At ordinary angles of friction this function amounts to about 25. So in the case of pneumatic tyres the tyre pressure, divided by 25, must not-exceed the initial yield stress, to avoid deformation of the carpet. This condition has to be met at every temperature, which can occur on the road, so that in this case this condition has to apply especially at the highest temperature.

In a large number of cases the mechanical analysis of the stresses in a construction will be very difficult. It is an experience in engineering practice that very often approximations must be allowed, giving rise to the introduction of smaller or larger safety factors in the final results.

For a fruitful development a simultaneous increase in precision of calculations and of the knowledge of the material is wanted. Whereas for pure bitumens and for mixtures of bitumen with filler and coarser material the knowledge of the material may be considered as being at about the same level as the development of mechanical analysis, it must be stated that for bitumen-filler mixtures the knowledge of the material is still in arrear.

Under dynamic conditions the picture becomes more complicated. In a number of cases the stress conditions will be probably less severe than under static loads (*e.g.*, a moving car on a road in comparison with a standing car), so that a calculation about the static case can suffice. In other cases, however, where high loads are applied for a short time (shocks) mechanical analysis becomes very inaccurate.

To give an idea about the stresses and their duration a steel ball falling from a certain height upon a thick bituminous layer will be considered. Assuming a modulus of elasticity of 10^{10} dn/cm^2 and ignoring mass effects and mechanical loss, it is found by calculation that at the point of maximum deformation shearing stresses of 10^7 to 10^8 dn/cm^2 are easily obtained, whereas the duration of the collision amounts to 10^{-2} to 10^{-3} seconds or less.

When considering the different kinds of application of bitumen in the above-mentioned ways, a rough division can be made according to Table II.

In this table the applications are divided according to the mechanical conditions to which the bituminous material can be subjected. In most applications shocks can be exerted upon the material, giving rise to high stresses for a short time. In other cases intermediate stresses can be applied for an intermediate time (bending of bitumized felts, of bituminous

duplex paper, or of bitumized cables), whereas in still other cases stresses can be applied for a long time; dependent upon the application these stresses can be low (bituminous layers in roofing felts), intermediate (damp coursing layers) or high (bituminous roads under static loads, pipe coating in stony surroundings).

TABLE II.

Mechanical Conditions of Different Applications of Bitumen.

Shearing Stress, time.	Low, $<10^3$ dn/cm^2.	Intermediate 10^3 to 10^5 dn/cm^2.	High, $>10^5$ dn/cm^2.
Short, <0·1 second			
Bitumen			Paints Adhesive layers
Bitumen + filler			Pipe coatings Thermoplastic moulded articles
Bitumen + filler + coarser aggr.			Road carpets Briquettes Joint-filling materials
Intermediate, 0·1–100 second			
Bitumen		Adhesive layers Roofing felts	
Bitumen + filler		Coatings for cables	
Bitumen + filler + coarser aggr.			
Long, >100 second			
Bitumen	Roofing felts Paints	Adhesive layers	
Bitumen + filler	Pipe coatings	Thermoplastic moulded articles Damp coarsing layers	Pipe coatings Damp coarsing layers
Bitumen + filler + coarser aggr.		Linoleum Briquettes	Road carpets Joint-filling materials

This Table is open to criticism being neither complete nor thoroughly descriptive of the applications mentioned. It only serves to show what conditions must be considered as the most important.

When comparing these mechanical conditions with those under which examination of bituminous materials has been carried out, it is found that further knowledge about the material is especially wanted about the following points:

(1) Behaviour of the materials under high stresses for short times (shocks). Besides the typical rheological properties, information is wanted about fracture phenomena. The methods described in the literature must be applicable to bitumen without special difficulties.

However, it must be stated that in most cases, as described in the literature, the amplitudes used are very small. Application of these methods to bitumen will give rise to stresses of the order of only 10^5 dn/cm^2, so 100 or more times less than those estimated for shocks of reasonable intensity in bitumen. Whereas the knowledge of elasticity

modulus and mechanical loss will open a number of new aspects, investigation at higher amplitudes may become necessary afterwards.

(2) Rheological properties of bitumen-filler mixtures. This point is especially of interest in the case of higher filler concentrations. In connexion with the high stresses which must be expected to be necessary, investigation by compression of rather long cylinders in the direction of their axis seems advisable.

(3) Rheological properties of pure hard bitumens. Here the main difficulty in the investigation lies in the low rate of deformation, so that long measuring times are necessary. A series of a simple type of viscometer, *e.g.*, the Pochettino (concentric translation) apparatus seems the most convenient.

Connexion Between the Mechanical Conditions of the Mixture and the Corresponding Conditions of the Bitumen Component.

The connexion between the mechanical conditions of a bituminous mixture and the corresponding conditions of the bitumen component has already been discussed in the first chapter. It was concluded that no direct connexion is obvious from the experimental facts. It is true that increasing softness of the bitumen is accompanied by a corresponding change in initial yield stress and viscosity of the mixture. However, other properties of the bitumen too seem to play an important part.

Investigations of bitumen-filler mixtures must be carried out before a better understanding can be obtained. In view of the situation as regards road building it must therefore be stated that when considering mixtures of the sandsheet- or asphaltic concrete-type the penetration of a bitumen does not give less useful information than a more extensive investigation by means of concentric rotation type of viscometers. On the other hand, in cases where the bitumen is wholly or partially present in a more or less pure state, as can be the case with surface treatments, a more precise investigation of the bitumen can give better information about road experiments. But even in the first case it must be considered highly desirable to collect more data on the rheological characteristics of bitumens used in road experiments in connexion with possible future developments; the choice of these data, however, is still arbitrary.

Discussion.

The Chairman (Dr A. R. Lee): I am not very clear in my mind whether Dr Saal's final conclusion was that we need not bother about the viscosity characteristics of the bitumen, because we shall never be able to relate them to the conditions on the road, or whether he said that we should carry on and do some more work on the subject; I think he said we should carry on and do some more work. I should be very disappointed to think that the flow characteristics of the road could not be related, to some extent at any rate, to the flow characteristics of the binder which is sticking the aggregate particles together.

There is no doubt, of course, that bitumen is a difficult rheological

material. If you consider tar, it is a simple Newtonian liquid, and if you double the stress on it you double its flow: if you take off the stress, the flow stops. A piece of rubber is a solid having very pronounced elastic properties, and when you load it and deform it, and then take off the load there is an elastic recovery and you can measure the load and the elasticity. But bitumen is a difficult material, and the difficulty is to sort out the various aspects and put them into their proper places. The mathematician and the physicist are in their element if they can get to grips with the subject; and I should certainly like to see some of the materials to which Dr Saal refers in his paper illustrated by details of his results. I am sure he must have a lot of results he could give in rather more detail.

For instance, there is the temperature susceptibility of the mixture, which is smaller than the temperature susceptibility of the bitumen itself. It would be interesting to see the mathematical explanation which may be behind that. I gather, from what Dr Saal has said, that it is related primarily to the stress/flow relations, and that in mixtures of bitumen and mineral aggregate the stress/flow relations are different from the stress/flow relations of the bitumen itself.

This question of correlation is most important, of course. One has a feeling that the repetition of a transient stress, such as is imposed on a road, is not just simply additive, but that there is something here which we do not understand; I welcome his suggestion that more work should be done on vibrational methods.

I would like to come back to the original question which prompted us to ask Dr Saal to review the position, and that is the simple question of the measurement of the viscosity of a bitumen. It is not a simple liquid; it has a most complicated flow characteristic; it possesses an elastic recovery property, it possesses a structural property, and it possesses a flow property. What we want it to do on a road is to remain in a stable condition and not to deform at all under traffic and temperature stresses; in other words, we are interested in the flow properties of the bitumens in the condition in which they do not flow, the condition just before they start to flow. That is a very difficult part of the curve to investigate, of course, the part before you get to the real curve. But this is a matter particularly worthy of investigation; how should we express the viscosity of a liquid just before it flows? Also, our experimental work has emphasized the need for further investigations of flow properties at temperatures of 0° C and lower.

DR SAAL: The first point raised by the Chairman is one which I mentioned, that the rheological characteristics of mixtures cannot be related with those of the bitumen itself; and the Chairman feels that a certain connexion ought to be there. But, as I explained, in our work we came to the conclusion that the bitumen, as it governs the properties of the mixture, is different from the bitumen before it was added to the mixture, because we think that a certain amount of adsorption of the bitumen takes place on the surface of the mineral aggregate, and that that adsorbed layer has an influence on the mechanical properties of the mixture.

Taking this hypothesis as a starting-point, it is clear that, even if there is some relation between the rheological properties of the pure bitumen and those of the adsorbed layer, other factors, such as the degree of adsorption, enter into the problem. Therefore, a clear relationship between the

rheological properties of the mixture and of the pure bitumen cannot be expected.

Why do we assume this adsorbed layer? The reason is that if we determine for the pure mineral aggregate the properties which I have indicated by initial yield stress, and then add a liquid to the system, there should be no change of this stress; but it is found that the value of this yield stress changes very considerably when the bitumen is added. That value is dependent on temperature, for instance. The only way in which we can explain this fact is to assume that at the points of contact, where the yield stress arises, the conditions have changed in a certain way. Change of adsorption is the most likely change.

Then the Chairman referred to repetitions of load, and said we should have to reckon that the effect of the first application of load will be different from subsequent applications. I quite agree with him, judging from the literature. People assume that there is a certain logarithmic relationship between the deformation and the number of applications of load, that is to say, that the first ten deformations have about the same effect as the next hundred, etc. I have no experience; but the indications from the literature point in this direction.

The Chairman has mentioned that we are in a very difficult position with regard to the properties of bitumen, because it has all the properties of deformation which can be imagined. Bitumen can show viscosity, certain elastic effects, and in certain cases time will assert its influence; the viscosity is reduced after a long-period application of stress. The elastic effect I have mentioned very briefly in the paper. It is very difficult to relate such properties in the pure bitumen to the properties of bituminous mixtures.

The last point mentioned by the Chairman concerns the influence of viscosity on the properties of the mixtures. As he stated, we like a bituminous carpet having no deformation at all. To obtain information about the properties of the material a mechanical vibration analysis can be made. For instance, a piece of the material can be vibrated, and if the experiment is carried out at different frequencies there will be a frequency at which the amplitude of the vibration is a maximum. It is possible to calculate the modulus of elasticity from that frequency and the dimensions of the test piece. As mentioned in the paper, this modulus of elasticity is different from the static elastic effect I have mentioned in connexion with viscosity. For instance, if you have a bitumen which shows no static elastic effect at all, and if you prepare a piece of the material and vibrate it, it is just as easy to determine its dynamic modulus of elasticity. So that we can say that this modulus of elasticity is a property which has nothing to do with the slow elastic effect.

In the vibration experiment the internal damping of vibration of the material is a property which can be determined. It is clear that there is a great difference in respect of the internal damping properties between different materials. For instance, if you subject a metal to vibration and then take away the external source of vibration, the vibration of the metal will continue for a certain time. On the other hand, in the case of rubber the vibration stops rapidly. It has to do with the internal friction of the material, which is high in the case of rubber and low in metal. In bitumen it can be measured in the same way as in rubber, and you come to the

conclusion that the internal damping property of asphaltic bitumen is high; in most kinds of bitumen it is higher than in rubber.

A large number of investigations has been made in order to calculate the internal friction, which must be the origin of the damping, in connexion with the ordinary viscosity of the material. Nobody has ever succeeded in putting forward a simple relationship between the two properties, and from the measurements that can be made at different frequencies it is easy to appreciate why there is this absence of relationship between damping and viscosity. It is found that the damping is independent of the frequency over a large range of frequencies, whereas one would expect that if the frequency is higher the damping effect will be higher. If you like to connect viscosity with the damping, you come to the conclusion that the damping must be proportional to the frequency; but there is no obvious relationship.

So that, to the Chairman's question as to whether there is any possibility of measuring the viscosity at the beginning of deformation, my answer is that you can measure a property which is of the character of viscosity, but is not directly related to the viscosity as found in the static rheological investigation of the material.

MR P. J. RIGDEN: In item (5) on page 71 of the paper the author refers to investigation of the behaviour of bitumen at temperatures below the range in which most investigators in the past have worked. I would like to say how much I agree with the author, for quite clearly we do want more information on flow properties and the other rheological properties at temperatures down to and below 0° C. We want investigations within the range from — 5° C up to perhaps 45° C; in the summer the temperature on the road goes up to about the latter figure, but the average over the whole year on the road is about 10° C. If we confine our investigations only to what happens in hot weather, we are not making a complete study of bitumen over the whole range of its service temperature. The author states in that item (5) that the behaviour of soft bitumens can be deduced from that of harder bitumens at higher temperatures. I would beg to differ very much on that matter. I think it is very dangerous to deduce the behaviour of one bitumen at 0° C from a knowledge of the behaviour of another at a temperature above 15° C.

Another point I would like to mention concerns the section of the paper dealing with bitumen-filler mixtures. The author refers there to the viscosity characteristics of those mixtures in relation to different ranges of concentration of filler. The Einstein law is referred to, but I am not clear what he means by "dilute suspensions." My experience is that Einstein's law breaks down very quickly when filler is added to tar or bitumen. It is stated in the paper that "no influence of shearing stress on viscosity has been found in these dilute suspensions." There again it depends on what is meant by "dilute." I would agree that, if in the first instance you have a bitumen in which the properties are not greatly affected by shearing stress, then if you add filler you do not perceive very much influence of shearing stress due to the addition of the filler until you reach a concentration of the order of 40 or 50 per cent for ordinary limestone dust filler.

The author refers to elastic recovery, or fore- and after-effect, which

may be produced by or may accompany the additions of filler to bitumen. As a matter of interest I would mention we have found recently that if you take an ordinary 60/80 pen bitumen which shows no elastic recovery in normal tests and then heavily load it with filler so that you have a solid material containing perhaps only 15 per cent of bitumen, that material shows very marked elastic fore- and after-effect. The question arises, whence does that recovery come? Does it come from the bitumen, which on the face of it does not show a recovery (although it may be a question of the fineness of your measurements), or does it come from the particle, which is a solid and, therefore, possesses elastic properties? I think it is more likely that it comes from the nature of the structure itself, the putting together of the two phases, solid and liquid.

The author has not touched on the mechanism of rupture and fracture in bituminous materials, but I think this is a very important property. We are apt to give rather a lot of attention to roads which deform badly and too little attention to the other aspect of road failure, that is the cracking or rupture, resulting in small pieces coming away, involving very often a rupture of the "mortar" part of the material. We are working on this question of the rupture of materials, and there is one particular point which has emerged from the investigation so far, again talking of mixtures rather than pure bitumen. Filler-bitumen mixtures show a rupture after being submitted to a stress which produces what is, apparently, ordinary flow. In other words, the mere fact of flow has produced a weakening of the material, and a rupture. If a tensile stress is applied which is less than the ultimate strength of the material, so that the material undergoes ordinary tensile strain, the material will break suddenly after a period of flow. What is happening to the material in the meantime to make it lose its cohesion and break? The answer lies in the existence of a void structure in the interior which has been opened out by virtue of the tensile stress; the material is progressively weakened until the applied stress exceeds the breaking stress. This is the phenomenon of volume flow which has been known always to rheologists but only recently has been demonstrated to exist.

On the question of measuring viscosity and studying flow in general, Dr Saal refers to the cylinder compression test. We are using a cylinder compression test for studying the properties of bitumens at fairly low temperatures, employing a cylinder about 1-inch long and ½-inch in diameter. This is a method I would like to underline, because I feel it is a much sounder method of testing, particularly when you are interested in what happens right at the beginning of a deformation, the point mentioned by Dr Lee. Apart from that point, it is much sounder mathematically to test the material in pure shear, i.e., shear unaccompanied by any rotation. Almost all other methods, capillary tube, concentric cylinders, rotating discs, and so on, involve rotation of the volume element. If you are testing an ordinary liquid it does not matter if you do rotate the volume element. But Dr Saal has pointed out that bitumen is not an ordinary viscous liquid; it is more complicated, and as soon as you have a material which has ordinary viscous flow properties and also elastic properties, which means that it may show quite large elastic deformation, which is recoverable, then by shear and rotation you find that the direction of strain for the

elastic part of the deformation begins to differ from the direction of strain for the viscous part. There is anisotrophy involved in between the viscous and the elastic elements, and that can account for curious phenomena which do not belong to the material at all.

DR SAAL: With regard to the necessity for making experiments at lower temperatures, and the statement I made in the paper that for soft bitumens the behaviour at low temperatures can be deduced from that of harder bitumens at higher temperatures, I quite agree that in that deduction there is an element of danger; but even if we have not at our disposal direct measurements of the viscosity and elasticity characteristics of bitumen at low temperature, we can get indirect information showing how far is the deviation from the expected behaviour. We have obtained this information from the change of penetration with time of penetration. Whilst I do not say that the deduction I have suggested is quite accurate, it has proved to be not very dangerous.

I think we agree that very little is to be found in the literature concerning the influence of filler. I mentioned in the paper the different behaviours of different fillers. So that from our experiments we can say that certain mixtures of filler and bitumen behave as one would expect, but that as soon as you begin to use filler particles appreciably deviating from a spherical form, deviation occurs.

I am very interested in Mr Rigden's remark that at higher concentrations of filler the mixtures show elastic properties. I am inclined to believe that this effect can be explained in the same way as we explain a yield stress in the bituminous concrete type of mixture, in that a certain coherence between the filler particles is formed giving appreciable elastic effects.

Then Mr Rigden mentioned the phenomenon of fracture. I have not mentioned that question in my paper because there is still little general insight into problems relating to fracture. In the case of mixtures of mineral aggregate with a liquid system such as bitumen, there is a possibility of connecting viscous properties of the binder with the tendency to fracture. I hope that when Mr Rigden has completed his experiments he will publish the results, for I think they will be very interesting to many people.

About testing methods, Mr Rigden has mentioned that he prefers to use compression or tension tests; and I agree with him that, in the case of hard materials, that is very effective. The investigations will especially lead to information about small deformations. In the case of softer bitumen a drawback is the difficulty to keep the material in shape during such tests.

MR J. F. T. BLOTT: We have used the compression method, but we have difficulty in interpreting the results. I think you will find that you have conditions of pure shear in only one plane in dealing with the purely elastic materials, but that with materials which are anomalous from the point of view of viscosity or elasticity it is very difficult to know what are the conditions obtaining.

What we are really interested in are the properties of the binder under conditions of strain such as are applied in practice. Those conditions of strains, I think, are small, whereas in the normal method of testing viscosity the measurements are usually made at much greater strain; very often the

bitumen "has its neck wrung," to get rid of the complications at the beginning, and make the matter simpler. Measurements made in this way bear little relation to the conditions to which the bitumen is subjected in practice.

Dr Saal has shown his enthusiasm for vibration methods of test. I wonder whether, in vibration tests, we go too far on the other side and impose strains much smaller than are normally imposed in practice. In that case we shall be studying the performance of bitumen in respect of the transmission of vibration rather than in relation to the conditions in which it has to serve on the road.

Dr Saal: The first point made by Mr Blott concerns the strain applied to deform bitumen in the course of the investigations. I quite agree with him that in general we are most interested in small strains, and that is a special reason why the emphasis must be laid, not only on viscosity, but also very considerably on the elastic effects which are found in the slow rheological investigation. Even if you measure with the viscometer strains which are appreciably higher than 1, you obtain information about the viscosity of the product. But I think that during the last ten years, when we have come to a closer study of the elastic properties, we have always discussed just the small strains far below 1.

With regard to vibration, in the normal methods which are used for the investigation of the dynamic modulus of elasticity, and damping, very small deformations are used. But it is possible to use a much larger amount of energy, so much energy that it can cause fracture of the material by vibration. We are doing that; so that we are trying to cover the whole range.

As to how far vibration work will be of importance for a close study of the factors relevant to the mechanical properties of the material in road construction, I think that much can be expected in this direction. But, of course, we can only be certain when we have enough information available to enable us to correlate the properties of the material with their behaviour in practice.

Mr E. Thornton: In connexion with the theory of adsorption, is it not possible to test it by making a viscometer test of the materials and then observing their behaviour when subjected to rotation, and so on, against other materials? It seems that we could test the theory by making a moving element of the solid and noting the difference between the observed results and those in the viscometer test.

Dr Saal: The question is how far we want to go into detail in connexion with the adsorption hypothesis. In research there is always a tendency to give a certain explanation of a phenomenon; we explain the phenomenon in this case by adsorption. But if we go into it more deeply I think it will take too much time and will direct our efforts into channels which are not of immediate importance.

Mr J. F. T. Blott: Have you any information on the effect of strongly adsorbed materials?

DR SAAL: If we have materials which are known to be strongly adsorbed, we know that the properties of the mixture can change.

MR A. G. WARD: I would like to take up the question of the damping coefficient. Dr Saal has mentioned that there is in fact no correlation between the damping coefficient and the normal viscosity, and that the damping coefficient is independent of the frequency. But surely the connexion should be between the damping coefficient in the vibration experiment and the manner in which the elasticity is developed in periods of the order of the vibration periods. That is to say, in order to find an analogy with normal non-reciprocating testing, you would have to conduct an extension or other form of experiment in which you are measuring the strain possibly in times of the order of one milli-second, or of ten or a hundred milli-seconds, according to the frequency of the vibrational testing. There is a possibility of developing a mathematical theory relating one set of results to the other. It is not a very satisfactory theory, in that it does not explain this peculiar independence of frequency; but it does give a connexion between the extension experiment and the vibrational experiment.

I should like to ask whether Dr Saal or anyone he knows has yet made any attempt to apply the Sack–Frolich theory to actual practical cases. So far as I am aware, there is no practical application of that theory; but I should like to know whether there is any hope that that theory can be developed and applied to the work.

On the question of volume change, I suggest that one should be rather cautious in applying the results, because the immediate consequence of having a material of this character is that you have to consider a hydrostatic pressure in addition to the shearing stress. The result is that those materials which will fail in tension at comparatively small deformation may at high compression pressure suffer shear without any sign of failure.

DR SAAL: With regard to the first question, I have seen in the literature a few references to the mathematical transformation of damping experiments or damping coefficients for a certain kind of spring-dashpot system. The difficulty in all these cases is that you get a formula, but I have never found that this gives a new aspect to the question. You can transform your measurements into some system with rather complicated properties, with a series of different relaxation times; but, as you indicate, that is not the solution of the problem.

The second question is how far we can apply the Sack–Frolich theory, which gives the stress in several parts of the construction as a function of the load applied. Calculations in which the theory is used have been made in connexion with the construction of airfield runway foundations.

The question with regard to volume change is difficult. If you deform a mixture with a pressure which is not too high you will find that, due to the deformation, the volume of the material increases; this increase of volume can give rise to fracture. The reason is that the particles shift over each other; to produce deformation, they must come apart to a certain extent, and that can be the beginning of rupture.

MR W. LETHERSICH: I am interested in Dr Saal's description of the measurement of the damping of bitumen by the method of vibration of rods. Some years ago I used a similar method and calculated the viscosity from the sharpness of the resonance curves. Like Dr Saal, I found that the values obtained did not agree with those predicted theoretically.

The explanation appears to be due to the existence of a volume viscosity. This was suggested by Frenkel and Obrastzov (*Jn. Physics*, 1940, II (2), 131). Changes in volume due to the hydrostatic stress component do not occur instantaneously, but are associated with friction. This friction is known as volume viscosity as distinct from the viscosity of damping due to elastic after-effect and plastic flow. At high frequencies the latter effects do not have time to operate, so that this volume viscosity is the predominant factor, and it is found theoretically that the viscosity is then independent of frequency. An interesting point here is that the damping decreases with increase of viscosity, but in the case of volume viscosity the damping will increase with increase of volume viscosity.

This subject is now being investigated fully by the Electrical Research Association in connexion with plastics.

With regard to Dr Ward's criticism of the use of mechanical models, I agree that when considering large strains they are not rigidly applicable owing to non-linearity; but when dealing with the small strains involved at higher frequencies the strains become linear with stress and the models do then represent the rheological properties of the material.

The models are useful, however, in that the existence of the dynamic and static elasticity modulii can be explained as well as other phenomena. In spite of non-linearity, the strains due to the various components of the model are superposable provided the stress is constant, so that one is able to analyse results by measuring strain/time relations at constant stress.

MR A. W. JARMAN: The layman has a difficult job to reconcile many of these arguments. Although they are no doubt very pertinent, he does ask himself how much further forward we may be when we have the next meeting of the Sub-Committee and can say that we have listened to Dr Saal and are met to consider which form of viscometer we are to propose. That was a major reason for asking Dr Saal to give the paper. I am a little consoled in my inability to determine between these various theories by the knowledge that they are all so violently contradictory; there is, perhaps, a possibility that the layman may find that his views are not so far out in the end. Far be it from me to decry the enthusiasm of my research colleagues who are investigating these things; the meeting has been worth my while to hear the merits of bitumen explained by our D.S.I.R. friends. But I do feel that we must seriously face up to the question as to how the less scientifically minded of us can interpret these various matters which have been debated.

They fall into two main categories. There was some enthusiasm on the part of some members of the Sub-Committee to have a test which measures the rheological properties or the viscosity of bitumen, and various suggestions were put forward with a view to doing that, but nobody seemed to agree as to whether the means suggested would measure what was wanted; therefore, we had this meeting. Can we say that, while knowledge

is accumulating, let us be satisfied with a simple instrument, so that for the next few years those concerned with the practical applications of bitumen can have some guidance as to whether they are using the right materials for their particular jobs? I have yet to find that such instruments have failed badly to provide a useful practical guide to the behaviour of the bitumen; indeed, when reading the paper I thought I could see a glimmer of hope that they can perform a useful service in this respect.

Secondly, to what extent can we justify anybody, having developed a new method of testing, using it for specifying the properties of bitumen? We have heard about bitumen having fore- and after-elastic effects. We might have many terms which will fall heavily on those who have to consult with the ultimate user and try to advise him which material to use and how to use it, without worrying too much whether the elasticity comes before or afterwards!

Perhaps I may indicate the sort of rheological problems which really do arise. Early this year I visited a London college where some huts had been put up, in which the students could carry on their studies. On the roof the contractors had used bitumen, and over that they had used roofing felt. But perhaps because the roofing contractors had not studied the rheology of their products, they used the wrong bitumen, which flowed down the cracks, and the students found it very disconcerting. I am not sure whether or not that is the sort of problem which rheology will ultimately solve, but if the contractors had used what was normally used they would not have had that trouble.

We may not know much about rheology, but experience may indicate that, keeping other factors constant, a change in the properties of the bitumen may have some advantage. I wonder whether, if we apply all these various theories, we may eventually be forced back into saying that we cannot use a certain material because it is too hard, another is perhaps too soft, and that we should use one in the middle; and then we come back very nearly to the point we have reached to-day.

So that I want to ask, if Dr Saal has to choose an instrument to-day for measuring the viscosity or the rheological properties of bitumen at ordinary temperatures, which will he choose? His guess is better than most of ours. Subsequently, having chosen his instrument and having been given two bitumens of different properties, will he be able to say as the result of the use of the instrument which bitumen is the better for a particular use?

DR SAAL: With regard to the question concerning which type of instrument I should like to choose for investigating which bitumen to use, I am inclined to say "the penetrometer." For bitumen to be used on the road, this instrument gives information about the viscosity and the elasticity effect, not very accurately, but sufficiently for practical application. Naturally, I see the need for more accurate instruments for fundamental research purposes.

As regards the second question, in laboratory work we can try to relate the different properties of the materials; we can determine the properties of the components in different ways, and we can compare them with the properties of other materials of the same nature. The final aim is to combine this information with a mechanical analysis of the construction to

predict the results that can be obtained with certain materials. At the present, this is still mainly done, as far as it is possible, by comparison with practical experience. But we can say that the development of a better knowledge of constructional materials has been of such importance in a number of other cases of engineering practice that it should prove equally important in this case. I think that a very small percentage of the money that is spent on road construction could be invested usefully in research, to enable us to reach a better understanding of all the factors in connexion with asphaltic bitumen.

MR J. F. T. BLOTT: I think that in the concentric cylinder type viscometer one could get a fairly exact idea as to whether a certain bitumen would or would not penetrate to a certain extent in a reasonable time.

THE CHAIRMAN: There falls to me the duty and pleasure of thanking Dr Saal for so interesting a paper. There is no doubt that he has put forward a lot of new ideas which must inevitably lead to further investigations, which in turn will lead us to a better understanding of our problems. I think the matter was put very pointedly by Mr Jarman; and in view of the further questions which Mr Blott and other speakers have raised, perhaps Dr Saal might have second thoughts and we may have another discussion at some other time.

It seems we all agree that if we are to understand what is happening we must know the stress conditions and we must as far as possible simulate those stress conditions in our laboratories. If we are dealing with static conditions, then we use static tests and stresses of the same nature; and for dynamic conditions we must clearly investigate the vibration of materials.

About twenty or thirty years ago, when Bingham was starting his school of rheology, he pointed out that viscosity was perhaps the most common property that was measured in the various industrial fields; but when an attempt was made to measure viscosity, the first thing one did was to consider in which part of the world one was situated, and to choose instruments according to the latitude and longitude, for instruments were different in one country and in another. We have certainly made progress since those days.

I invite you to show your appreciation of Dr Saal's most interesting paper.

(The vote of thanks was duly accorded, and the meeting closed.)

INCENDIARY FUELS FOR VARIOUS PURPOSES.*

By C. M. Cawley,† J. H. G. Carlile,† J. G. King,† and F. E. T. Kingman.†

Summary.

An account is given of some of the work carried out at the Fuel Research Station for the Mixtures Committee of the Petroleum Warfare Department. The incendiary fuels studied were distinguished from pyrotechnics in containing a petroleum oil as a major constituent, and were devised as fillings for fougasses, mortar shells, incendiary shells, and air-dropped bombs, and for other purposes.

The Mixtures Committee, an advisory committee of the Petroleum Warfare Department from 1940 to 1946, was concerned with the devising, investigation, and development of incendiary mixtures for use in a wide variety of munitions of war. The Committee was formed in the summer of 1940 under the chairmanship of the then Director of Fuel Research, Dr F. S. Sinnatt, and from that date until the end of 1945, at least one team, and often two or more teams, worked continuously at the Fuel Research Station for the Committee. In addition, a considerable amount of work was carried out at the Station directly for the Petroleum Warfare Department.

Dr F. S. Sinnatt was chairman of the Mixtures Committee until his death in January 1943. Prof Sir Alfred Egerton was chairman from the spring of 1943 until March 1946 when the Committee was disbanded.

Various members of the Committee carried out research and development work on different projects. The most important work carried out at the Fuel Research Station was the study of the preparation and properties of fuels for flame-throwers, and in particular the creation and development of the aluminium stearate petrol gels known as FRAS fuels; this work is described in two papers.[1,2]

In addition, experimental investigations were carried out at the Fuel Research Station on the preparation and properties of incendiary mixtures as requirements arose from time to time in the Petroleum Warfare Department for mixtures or fuels for mortar-shells, air-dropped bombs, and other purposes. Some of the results of this work are summarized in the present paper.

The incendiary mixtures devised and studied were for the most part distinguished from pyrotechnics in that a petroleum oil was almost always a major constituent of the type of mixture examined. The first requirement, in late 1940 and early 1941, was for a fuel for the fougasse, mortar, and flame barrage which would burn without the production of smoke. A little later, a mortar-shell incendiary fuel having a high anti-personnel value was required, and in the summer of 1941, work was carried out to assist the Mixtures Committee in its consideration of reports that the enemy was using spontaneously-inflammable incendiary powders. At

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† Fuel Research Station, Department of Scientific and Industrial Research.

about the same time, there was a requirement for an incendiary filling for air-dropped bombs. The work on flame-thrower fuels occupied the Fuel Research Station group for the greater part of the remaining war period although small requirements continued to arise, such as that for incendiary shell fillings about a year later. An igniter for highly viscous flame-thrower fuels was required in 1944, and in the same year there was a requirement for a means of obscuring the vision from enemy pill-boxes. The development of such projects was often cut short by the changing needs of the war, but it is of interest to put some of the results on record.

Part I.—Smokeless Incendiary Mixtures.

The counter-invasion measures developed by the Petroleum Warfare Department early in the war involved the production of incendiary fuels for mortar-shells and fougasses, and for the flame barrage. These fuels, based on petroleum and tar-products, emitted large volumes of smoke on burning, and for certain purposes this was undesirable. Investigations were therefore carried out to determine the possibility of producing alternative fuels which would burn smokelessly or with a greatly reduced emission of smoke.

Mortars and Fougasses.

The first requirement was for fillings for mortar-shells and fougasses and advantage was taken of the fact that at low temperatures (— 10° C) it is possible to make a gel with nitrocellulose in alcohol. Further work showed that a mixture of 40 per cent alcohol and 60 per cent petrol could be used without undue production of smoke on burning or breakdown of the gel structure. The nitrocellulose gel method was not entirely satisfactory owing to the necessity for using a low temperature of preparation, and though it was found possible to prepare a suitable gel at room temperature by using ethyl acetate instead of alcohol, it was found that ethyl acetate was not likely to be available in the required quantities. Tests were accordingly made on sodium stearate gels in alcohol and the alcohol–petrol mixture, and these fuels were found to be satisfactory, particularly when the gel was reinforced by the addition of rubber latex. All the mixtures described were tried out in 40-gal fougasse drums, and the composition of the mixture finally selected for fougasses was as follows :—

60 gal Pool petrol;
5 gal rubber latex;
40 gal ethyl alcohol;
25 lb stearic acid;
7 pints caustic soda solution (sp. gr. 1·43).

The latex was dissolved in the petrol and the caustic soda added with stirring. Meanwhile, the stearic acid was dissolved in the alcohol at 60° C and the solution then added to the petrol mixture. Stirring was continued for 10 minutes and the temperature raised to 40° C, after which the mixture was poured into the fougasse drum where it set on cooling to a heterogeneous gel.

In the field trials which were carried out, the combustion was nearly smokeless and the target effect was excellent.

Some experiments on mortar-shell fillings were also made using a nitrocellulose gel in ethyl acetate and petrol with the addition of 20 per cent white phosphorus. Tests in 5-gal mortar-shells gave good results, and the fuel burnt without producing black smoke, but the project was abandoned at this stage owing to supply considerations and the lack of any urgent need for smokeless mortar fillings.

Part II.—R.S.P. Anti-Personnel Mortar Fuel.

Early in 1941, interest in mortar fuels became very strong, and in particular there was a special demand for an incendiary filling with a high anti-personnel effect for the Newton long-range-projectile mortar. The projectile was a standard 5-gal oil drum fitted with an internal bursting charge and a gas check. The specification for the fuel required that (1) it should burn fiercely and should be difficult to extinguish, (2) it should adhere firmly to clothing or flesh and not be easily brushed or wiped off, and (3) it should inflict burns which would render the victim a casualty for a prolonged period.

A variety of mixtures was devised and examined and the mixture finally developed consisted of a rubber–petrol solution containing finely-dispersed, solid, white phosphorus.[3] The method of preparation of the mixture was to add a nearly saturated solution of white phosphorus in carbon disulphide to a solution of rubber in petrol (with constant stirring) so that the phosphorus was precipitated in a finely-dispersed condition. The particle size of the phosphorus could be controlled to some extent by the rate of addition and the rate of stirring, but was normally in the range 0·01 to 3 mm diam with the majority of the particles about 0·5 mm diam.

The suspension of phosphorus in rubber–petrol solution was highly viscous and on standing became still more viscous, finally setting to an elastic gel which could not be worked and flowed only with difficulty. The phosphorus settled rapidly at first, but the mixture appeared to attain a stable state when the volume of the layer of phosphorus was about half the total bulk. The concentration of phosphorus employed in the mixture was normally about 15 per cent; at lower concentrations the phosphorus settled to such an extent that ignition of all the mortar fuel on fragmentation could not be ensured, and at higher concentrations the mixture was too stiff to handle.

Effect of Additives.

The effect of additives was examined with a view to (1) stabilizing the suspension of phosphorus, and (2) facilitating the break-up of the mature elastic gel on projection from the mortar drum. Amongst the additives used were sawdust, sulphur, nitrocellulose, and vulcanized-rubber powder. Sawdust appeared to possess the greatest practical value in reducing the settlement of the phosphorus. It did not stabilize the suspension completely, but had the effect of increasing the bulk of the settled solids to two-thirds of the total bulk; in addition, it considerably facilitated the break-up of the gel on explosive discharge from the drum. Vulcanized

rubber stabilized the suspension completely, but produced a fuel too tough and viscous to be of any practical use for the purpose required.

Composition and Production of R.S.P. Gel.

The final fuel, containing 2 per cent sawdust and designated R.S.P. Mark II had the following composition :—

	Per cent by wt
Pool petrol	76·1
Crêpe rubber	4·1
Phosphorus	15·0
Carbon disulphide	2·8
Sawdust	2·0
	100·0

Sp. gr. at 15° C = 0·86

The rubber solution was prepared by dissolving 4 per cent wt/vol of crêpe rubber in normal Pool petrol. The concentration of the solution of phosphorus in carbon disulphide varied according to the atmospheric temperature from 8 g/ml at 15–20° C to 6 g/ml at 0–5° C, so that there were slight variations in the concentration of carbon disulphide in the final mix. The sawdust was the commercial variety prepared from soft wood; the specification stipulated that it should be clean and dry, containing not more than 20 per cent moisture, and that it should contain no particles larger than $\frac{1}{8}$ inch and not less than 60 per cent should be between $\frac{1}{8}$ and $\frac{1}{32}$ inch.

The production of this fuel, which showed promise of being a highly effective anti-personnel agent, was developed to the semi-technical scale and 1000 5-gal drums were filled for field trials. The mixture was made up in 50 to 60 gal batches in a closed tank fitted with a stirrer. The rubber solution was stirred and the sawdust added (in 5 minutes). Stirring was continued for a short period (5 minutes) and the phosphorus solution (previously made up and stored under water) added (in 5 minutes). The stirring was continued for a further 5 minutes after which the mixture was blown direct into the mortar drums.

When the rubber supply position became critical after the fall of Malaya, it was found possible to replace the rubber–petrol solution by a 10 per cent solution of perspex in benzole without any material change in the properties of the mixture (other than the specific gravity and hence the total weight of the charge). This filling was known as P.S.P.

Ignition of Fuel.

On explosive discharge from the drum the charge was distributed as small blobs which clung tenaciously to the target and burnt fiercely, the effect of the burster charge being sufficient to ignite most of the fuel. Quantities of about 1 kg burnt for about 10 minutes. In the absence of immediate ignition, spontaneous ignition would occur after a delay period, the length of which depended on factors such as humidity, temperature, wind, etc. A large number of experiments were carried out on the spontaneous ignition of R.S.P. in the open and while it was obviously dependent on the weather conditions, it was not possible to establish any simple

correlation between the time of ignition and the atmospheric conditions. It was shown, however, that the time of ignition was shorter when the R.S.P. fell on materials such as straw or even green grass than on bare ground, an effect due probably either to a " wick " effect of such materials or the possibility of the production of friction by the movement of the straw or grass.

Assessment of Effect of R.S.P.

The anti-personnel effect of materials such as R.S.P. depends to a large extent on their effectiveness in burning through clothing. A simple cloth-burning test was therefore devised for assessing the relative efficiencies of various incendiary materials.

The cloth used was standard British Army serge and the apparatus consisted of a metal ring (6 inches diameter) fitting loosely in a circular hole in a wooden board; the test-piece of serge was stretched over the metal ring, which was then pressed tightly into the wooden frame. The frame was supported in a horizontal position and the incendiary material (0·1 g in weight) in the form of a " slug " 0·3 to 0·4 inch long was placed on the cloth and ignited. The time of the appearance of flame through the cloth was noted, and after combustion had ended, all badly charred cloth was removed and the size of the resultant hole measured. Results for white phosphorus, P.S.P. containing various proportions of phosphorus but omitting the sawdust in order that representative samples of 0·1 g could be taken, and FRAS flame-thrower fuel (*i.e.*, petrol gelled with aluminium stearate) are given below in Table I.

TABLE I.

Effect of Various Fuels in Cloth-Burning Test.

Incendiary material.	Time taken to burn through cloth, sec.	Diameter of hole, cm.
White phosphorus . . .	7	3·3
P.S.P. (15% P) . . .	21	1·4
" (25% P) . . .	14	1·9
" (50% P) . . .	9	2·0
" (60% P) . . .	9	2·6
FRAS fuel	Cloth charred, but no hole through	1·8

White phosphorus was the most effective of the materials tested, and in the series of P.S.P. fuels the effectiveness increased with the concentration of phosphorus. Gelled petrol was much less effective. The comparative ineffectiveness of the gelled fuel was shown more clearly by results obtained with double thicknesses of cloth. White phosphorus burnt through two layers of cloth in 20 seconds, making a hole 2·3 cm in diameter in the second layer, whereas FRAS fuel failed even to scorch the second layer. The P.S.P. fuels gave intermediate results in accordance with their respective phosphorus contents. It cannot be deduced from these results that phosphorus alone would necessarily be preferred to P.S.P. or R.S.P. as an anti-personnel agent since the greater time of burning of the latter fuels

and their plastic consistency and adhesiveness offer certain advantages to counterbalance the fiercer burning of phosphorus.

Part III.—Incendiary Mixtures for Bombs and Shells.

Mixtures for Air-Dropped Bombs.

A lengthy series of experiments was carried out during 1941–42 on the development of incendiary mixtures for air-dropped bombs. The primary object of the investigation was to provide a substitute for the magnesium bomb, in view of a threatened shortage of magnesium and aluminium; it was therefore essential that neither of these two metals should form a constituent of the mixtures except possibly in a very small proportion.

It was decided that, in general, the mixtures should be made up to comprise an oxidant, a reducing agent, and a fuel; it was thought that the reaction between the first two should give a fierce fire while the fuel should provide an extended period of combustion. Lists of materials examined are given below, the distinction between reducing agent and fuel is of necessity somewhat arbitrary in some cases.

Oxidant.	*Reducing agent.*	*Fuel.*
Sodium nitrate.	Sulphur.	Pool petrol.
Red lead.	Magnesium.	Kerosine.
Barium nitrate.	Aluminium.	Paraffin wax.
Sodium peroxide.	Charcoal (powdered).	Rubber–petrol solution.
Sodium permanganate.	Coal (powdered).	Rubber–kerosine solution.
Potassium chlorate.	Low-temperature coke (granular).	Rosin.
Ammonium dichromate.	High-temperature coke (granular).	Vertical retort tar.
Ammonium nitrate.	Phosphorus.	Coal-tar pitch.
Nitrocellulose.	Silicon.	Sawdust.
	Calcium silicide.	
	Ferrosilicon.	
	Iron filings.	
	Pyrophoric iron.	

Testing of Mixtures.

Preliminary tests on all mixtures were made in 100-g samples burnt on wooden or metal plates, the mixtures being ignited by a fuse, or in more difficult cases, by a fuse with 1 per cent of an easily ignited mixture as a primer. Any promising mixtures were then burnt in 1 kg batches on a wooden structure, of which there were two types. Type A (Fig. 1), consisting of a wooden baseboard, with a simple superstructure, was designed to provide the means of measuring the total incendiary power of the mixture and was used extensively in the early experiments. Type B, on which most of the later tests, the results of which are quoted in this paper, were carried out, consisted of a wooden baseboard made to simulate a section of floor boarding. This latter type of test structure was preferred since it was felt that the test of the capacity to burn downward through a wooden floor rather than the capacity to ignite an inflammable structure which might not be present in practice, would give the better assessment of the relative merits of various mixtures. Both types of structure were raised 4 inches above floor level for the purposes of the test.

Summary of Results.

(*a*) The best oxidant tested was sodium nitrate; sodium peroxide was too unstable in the presence of traces of moisture, while ammonium and barium nitrates were less effective.

(*b*) Throughout this work it was found that the wooden baseboard used in the tests did not continue to burn for any length of time after the incendiary mixture itself had burned out. The fire caused by these mixtures was thus in marked contrast to that caused by the magnesium bomb, a difference which must be attributed to the difference in the residues left

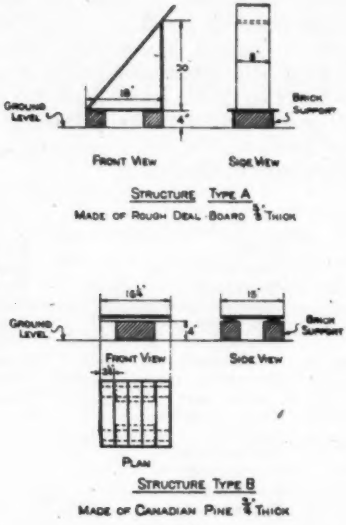

FIG. 1.

WOODEN STRUCTURES FOR BURNING TESTS.

on combustion. The magnesium bomb leaves a voluminous porous mass of magnesia (m.p. 2800° C) whereas the mixtures examined in this work usually left a fused slag, due to the presence of materials with low melting points and, in particular, sodium salts with melting points varying from 316° C for the nitrate to 1088° C for the silicate. The low fusion points of the residues detracted considerably from the value of the mixtures since the fused residue acted as a protective layer to the wood and prevented further vigorous combustion once the incendiary mixture itself had burnt out.

(*c*) It was thought that iron might prove a useful constituent of incendiary mixtures, in spite of its low thermal value, since it left as a residue a very hot slag which might prove an effective incendiary weapon. Mixtures were therefore made up containing varying proportions of iron of a range of particle size from iron filings to pyrophoric iron. The mixtures left a bright red-hot slag which remained visibly hot for several minutes,

but as already shown, non-porous slags are not desirable and the hot residues were not particularly successful as incendiary agents. Some study was also made of ferrosilicon which burns more fiercely than iron and leaves a hotter slag. This work included some tests on ferrosilicon briquettes (with the addition of sodium nitrate, Fe_3O_4 and charcoal). While these fuels were slightly more effective than those containing iron, the general conclusions as to the ineffectiveness of iron and to a lesser extent of ferrosilicon, as additives to incendiary fuels, mainly because of the nature of the residues, remain unaltered.

TABLE II.

Combustion of Various Mixtures.

Mixture no.	FR47 (with primer).	FS30.	FM32.	FM37.	Magnesium bomb.
Composition (per cent by weight):					
Low-temperature coke (through ⅛ inch)	4	—	—	—	
Calcium silicide	—	60	37	—	
Silicon	—	—	—	38	
Magnesium, grade 5H	—	—	37	38	
Sodium nitrate	77	15	6	4	
Rubber–petrol	19	25	20	20	
Bulk density, g/ml	1·5	1·5	1·1	1·1	
Thermal value, cal/g	2280	4880	5760	7280	Ca 6000
Combustion Tests (on type B wooden structure):					
(1) Time to reach fierce stage, sec	15	—	35	10	40
(2) Time of fierce burning, sec	500	90	85	90	over 660
(3) Time before wood burnt through, sec	240	—	330	300	270
(4) Loss in weight of wooden board, g	460	450	590	690	— *

* Practically completely burnt.

(*d*) The most effective fuel for compounding with the oxidizing and reducing agents was a solution of rubber in petrol or kerosine. It had a high thermal value (11,000 cal/g), and its use decreased the rate of burning and correspondingly increased the time of burning, so that variation in the rubber–petrol content of a mixture formed a useful method of controlling the combustion characteristics of the mixture.

(*e*) The most effective reducing agents were low-temperature coke, silicon, and calcium silicide. Mixtures containing only low-temperature coke, $NaNO_3$ and rubber–petrol gave a type of mixture which may be described as a flame producer. When, however, an excess of sodium nitrate was present (*i.e.*, when this constituent was appreciably more than half the mixture), it melted and flowed from the mixture to attack any combustible substance with which it came into contact. This type of mixture appeared to possess useful possibilities although it was recognized

that the considerations outlined under item (*b*) might condemn any mixture containing sodium nitrate.[4]

(*f*) The mixtures containing calcium silicide and silicon were probably the best of the substitutes for the magnesium bomb, and had the advantage of leaving a fairly porous residue on combustion which permitted combustion of the wooden baseboard to continue after the incendiary mixture itself had finished burning.

Some brief results of tests of 1 kg of the mixtures containing low-temperature coke, silicon, or calcium silicide with sodium nitrate and rubber–petrol solution are given in Table II, together with the comparable results for a 1 kg magnesium incendiary bomb.

Even the best of the substitute fuels was considerably inferior to the magnesium bomb. It was considered, however, that a mixture containing calcium silicide should have useful incendiary properties.

Incendiary Shell Fillings.

At a considerably later date, there was a requirement for an incendiary filling for the 3-inch howitzer and mortar-shells. It was required that the filling should :—

(1) Burn fiercely as a coherent mass.
(2) Have a bulk density of 1·25 g/ml.
(3) Not contain phosphorus.
(4) Not require the use of materials in short supply, especially rubber and magnesium.

The mixtures containing calcium silicide and sodium nitrate with rubber–petrol as a binding agent, described above, appeared to be suitable for this purpose provided that the bulk density could be lowered to 1·25 and that a suitable substitute could be found for rubber–petrol as the binding agent.

The effect of additives on the bulk density was first studied, and sawdust, wood shavings, wood wool, slag wool, cotton linters, and sisal were tested; it was found that cotton linters and sisal were particularly effective. Both these materials and particularly the cotton linters were of value in binding the mixture into a coherent mass and the use of sisal enabled a wide variation of density to be achieved by varying the degree of compression of the resultant stringy mixture. It was decided to use a combination of both additives, the amounts being 0·5 to 1·5 per cent of sisal and 1 to 2 per cent of cotton linters; the proportion of the latter material was varied in order to obtain the same consistency in the different mixtures examined.

The rubber solution was replaced, in the first instance, by heavy oils such as Pool fuel oil with the addition of 20 per cent petrol, but these mixtures were difficult to ignite, and a satisfactory substitute for rubber–petrol was found in a solution of perspex in benzole. Later it was found that another solution to the problem was to make use of the high absorptive properties of powdered aluminium to make suitable mixtures without thickening the petrol; the combustion properties were adjusted by the addition of magnesium, the supply position having eased during the course of the work. Four mixtures were finally selected for trial; the compositions and results of burning samples of 500 g at an air temperature of 0° C are given in Table III.

As a result of field trials using incendiary shells it was concluded that the best mixture for fierceness and continuity of burning was No. 117. No. 119 was interesting in showing the value of antimony trisulphide in facilitating the ignition of the magnesium; this mixture attained fierce combustion far more quickly than any of the other mixtures. The function of metal sulphides is dealt with more fully in Part VI.

TABLE III.

Burning Tests on Shell Fillings.

Mixture no.	100.	101.	117.	119.
Composition (per cent by weight):				
Calcium silicide	50	33	24	—
Magnesium, grade 5H *	—	17	5	17
Aluminium	—	—	15	—
Antimony trisulphide †	—	—	—	33
Sodium nitrate	20	13	16	13
Sulphur	2·5	2·5	2·5	2·5
Sisal	1	1·5	1	1
Cotton linters	1·5	1·0	1·5	1·5
Pool petrol	—	—	35	—
Perspex–benzole solution (4 per cent by wt)	25	32	—	32
Thermal value, cals/g	4200	5400	6400	4600
Burning Test:				
Time to reach intense burning, sec.	7	8	15	1
Total time of burning, sec	25	22	40	21

* This is a commercial grade, containing 50 per cent material passing a 240-mesh B.S. sieve.

† A commercial sample, ground to pass a 72-mesh sieve.

Incendiary Powders.

At one stage of the war, following a rumour concerning enemy activity with incendiary powders, information was required as to the possibility of the production of a fine powder which could be used in air-dropped containers (or alternatively, could be sprayed from aircraft or projected from a flame-thrower) and which would inflame spontaneously on exposure to air for a short period. It was decided to carry out a short investigation on this subject, during which numerous mixtures were examined, and at least two possible methods were devised for producing spontaneously-inflammable powders. The two methods of promise were:—

(1) The impregnation of magnesium powder (grade 5H) with phosphorus.

(2) The mixing of magnesium powder with pyrophoric iron or cobalt.

The first method consisted simply in mixing magnesium powder with a solution of phosphorus in carbon disulphide and evaporating the solvent. The mixture ignited on exposure to air after a short period—the length of which was controlled by the amount of carbon disulphide remaining in the powder. Alternatively, the phosphorus was impregnated on an inert diluent, such as magnesia, and the powdered magnesium and magnesia

mixed as required. This latter method facilitated the storage and handling of the powders, and again the delay period before ignition could be controlled by variation in the amount of carbon disulphide left in the magnesia.[5] This effect is illustrated by the results of experiments on the ignition of magnesia impregnated with phosphorus (10 per cent by wt) when exposed to air at 18° C (Table IV).

The normal composition of the mixtures used was 80 per cent magnesium and 20 per cent magnesia impregnated with phosphorus (5 per cent by weight of the magnesia). This mixture ignited satisfactorily at all temperatures above 15° C but failed to ignite at lower temperatures.

This fact would seriously limit the use of the phosphorus-containing mixtures and attention was therefore turned to the use of pyrophoric metals,

TABLE IV.

Effect of Carbon Disulphide in Phosphorus-Containing Powders.

Amount of carbon disulphide, per cent by weight of magnesia.	Delay time, sec
11·9	89
9·1	59
4·3	42
1·9	15
0·5	1
0·2	Instantaneous ignition

particularly iron, in effecting the ignition of powdered magnesium. Pyrophoric iron was obtained by the reduction of ferric oxide powder with hydrogen at 540° C. When pyrophoric iron was mixed with magnesium powder, the mixture flashed off brilliantly within 1 to 3 seconds on exposure to air. No experiments were carried out on the effect of temperature on ignition, but since it is known [6] that pyrophoric iron ignites spontaneously at temperatures down to — 78° C, it may be assumed that these mixtures would ignite at any normal atmospheric temperature. Mixtures were made with Fe–Mg ratios varying from 4 : 1 to 1 : 2; with a high proportion of iron the mixture burnt instantaneously, but with a high proportion of magnesium the mixture continued to burn in the manner characteristic of magnesium. One drawback to the use of pyrophoric iron as the ignition agent was that it did not retain its pyrophoric character on storage unless rigorous precautions were taken to exclude all traces of oxygen.

Pyrophoric cobalt was prepared by the reduction of cobalt oxide (obtained by the calcination of cobalt nitrate) at 300–340° C. It was rather more readily prepared than pyrophoric iron and was less liable to lose its pyrophoric character on storage in the presence of traces of oxygen. Reduced nickel was prepared in a similar manner to cobalt, but was only feebly pyrophoric and much inferior to either pyrophoric iron or cobalt.

PART IV.—SOLID INCENDIARY FUELS—"PYROTECHNIC IGNITER."

The work described in this part was originally undertaken to provide an igniter for thickened flame-thrower fuels to be projected from aircraft,

possibly at low temperatures. The properties originally required in the igniter were that it should :—

(1) Burn fiercely—a 4-inch length to burn for 10 seconds;
(2) Have a high thermal value; and
(3) Possess sufficient mechanical strength to remain in the form of a cylindrical tube (¼-inch walls) to surround the flame-thrower nozzle.

Following the results of earlier work on pyrotechnics and some American work on underwater flares, it was decided to use a mixture of aluminium and magnesium with sodium nitrate together with a binder to modify the explosive reaction between sodium nitrate and magnesium and to confer the necessary mechanical strength on the igniter. As a result of the examination of various materials, including coal-tar pitch, paraffin wax, "slack" wax, butyl phthalate, and lead naphthenate, a mixture of lead naphthenate and paraffin wax was chosen for use as the binder.

Commercial grades of materials were used, relevant data are as follows :—

Sodium nitrate. This was thoroughly dried and ground to pass a 100-mesh B.S. sieve.

Magnesium. Grade 5H.

Aluminium. 80 per cent passing a 170-mesh B.S. sieve.

Paraffin wax. M.p. 60–65° C.

Lead naphthenate. The sample (30 per cent Pb) was supplied by Messrs. Alchemy Ltd., Belvedere, Kent. Its calorific value (determined in a bomb calorimeter) was 6100 cal/g.

On the small scale the igniters were made up by mixing up the ingredients in the form of a paste with benzene, the mixture was cast into the necessary moulds or frames, and the benzene removed by heating in a vacuum oven.

The igniter was produced in two forms. In the original form the pyrotechnic material was packed between coaxial tubes, the inner tube of $\frac{1}{16}$-inch iron-wire gauge and the outer of steel plate perforated with ¼-inch holes. The diameter of the inner tube was ⅞ inch and the outer 1⅜ inch and the tube was 6 inches long. With Mixture 1 (see Table V) this annular container gave a burning time of 5 seconds, and with Mixture 4 a time of 13 seconds.

This type of igniter was designed to fit over the nozzle of the flame-thrower and was in fact used for this purpose in experimental work with success. It was, however, found impossible to use the igniter in practice, for reasons connected with the aircraft, and it was therefore proposed to use the igniter in stick form; the required time of burning was fixed at 6 to 7 seconds. Tests were carried out on various mixtures, cast in rods of two sizes, both 6 inches long and of square cross-section, one ⅞ inch square and the other 1¼ inches square. The results are given in Table V.

Mixture 2 was judged to be the most satisfactory; it burnt fiercely but steadily without any tendency to explosion. There was not a great deal of difference in the performance of the two sizes of sticks, but the larger burnt rather more evenly and rapidly, and would probably be more satisfactory on this account.

TABLE V.

Composition and Burning Properties of Pyrotechnic Igniters.

Mixture no.	1.		2.		3.		4.	
Composition (per cent by wt) :								
Magnesium	17·5		16·9		16·5		15·2	
Aluminium	13·0		12·6		12·3		11·4	
Sodium nitrate	49·5		48·0		46·3		43·4	
Paraffin wax	12·0		15·0		16·6		20·0	
Lead naphthenate	8·0		7·5		8·3		10·0	
Calorific value, cal/g	3700		3900		4100		4400	
Burning Properties of Sticks :								
Cross-section of stick	¾ in sq.	1½ ins sq.	¾ in sq.	1½ ins sq.	¾ in sq.	1½ ins sq.	¾ in sq.	1½ ins sq.
Weight of stick, g	70	140	70	140	85	150	100	200
Burning time, sec	4	4	7	9	7	10	8	12
Remarks :	Very fierce burning, sometimes, with explosive violence.		Steady, fierce burning.		Slow burning in initial stages.		Rather less easy to ignite and slow burning at start.	

PART V.—INCENDIARY MIXTURES FOR PRODUCING OBSCURATION BY FLAME.

Early in 1944, there was a requirement for a method for obscuring the vision from enemy pill-boxes and low-lying bunkers, and particularly for covering the advance of an attacking force from distances smaller than the range of a covering barrage to within the range of short-range weapons such as flame-throwers. The use of phosphorus smokes for this purpose had many disadvantages particularly as it was necessary that there should be no hindrance to the attacking force once the advance to the strong point had been covered.

It was intended that the obscuring agent would be fired in projectiles with a capacity up to about 10 gal, and it was suggested that the desired object would be achieved if the projectiles were filled with foam-producing chemicals which on explosive discharge from the projectile would produce a large volume of stable foam obscuring the embrasures; it was essential that this foam should be reasonably stable to simple counter-defensive measures by the enemy.

An alternative method of producing obscuration was suggested by the Fuel Research Station: this was to use an incendiary mixture leaving a voluminous ash. Complete obscuration would be effected for a limited period by the flame itself and the ash, if sufficiently voluminous, would afford some measure of obscuration, without any serious permanent hindrance to the attacking force. Any attempts to disturb the burning mixture or hot ash by the defenders would be difficult if not actively dangerous, owing to the pyrotechnic nature of the solid additives.

Earlier work (Part III) had shown that certain mixtures, containing magnesium, calcium silicide, and sodium nitrate, with rubber–petrol solution as a binder, gave bulky residues on ignition, but further tests on these mixtures showed that they were not adequate for the requirements called for in this work. Thus, when burnt in 100 g samples the time of burning was only 30 to 60 seconds and the swelling ratio, *i.e.*, the ratio of the volume of the ash to that of the original material, was only 2 to 3 : 1.

Further experiments were therefore carried out with mixtures of magnesium and antimony sulphide without any oxidizing agent. This mixture would be suitable for mixing with a gelled petrol, such as FRAS flame-thrower fuel, if necessary, as it contains no substance leading to the breakdown of such gels, but for certain practical reasons rubber–petrol solution was used as the binding agent. Attempts were made to increase the volume of the ash by the addition of mercurous chloride, mercuric thiocyanate, and

TABLE VI.

Composition and Combustion Characteristics of Mixtures for Obscuration.

Number.	F.M.1.	F.M.7.	F.M.8.
Composition (per cent by wt) :			
Rubber–petrol solution	35	35	35
Magnesium (grade 5H)	30	25	20
Antimony sulphide (through 72-mesh B.S. sieve)	30	25	20
Sodium bicarbonate	5	10	5
Hard coal-tar pitch (pulverized)	—	—	10
Sodium nitrate	—	—	10
Burning Tests :			
Burning time (fierce)	2 minutes	3·3 minutes	1·6 minutes
Swelling ratio	6–7	10–12	5–6
Nature of residue	Soft.	Moderately hard, very swollen.	Very soft.

sodium bitarbonate; the most effective of these substances was found to be sodium bicarbonate which not only gave the highest swelling ratio, but markedly increased the efficiency of combustion and eliminated the formation of black smoke. The effect of pulverized pitch was to lengthen the period of burning. The results obtained by burning 1-gal samples of three of the most effective mixtures are shown in Table VI.

The addition of sodium nitrate was deleterious from the point of view of the swelling ratio and the nature of the ash. Sodium nitrate has the further disadvantage that it destroys the structure of aluminium soap gels which it might be necessary or convenient to use.

Larger quantities of F.M.1 and F.M.7 were made up and burnt in 5-gal samples with the following results :—

*F.M.*1. A fierce flame 4 to 5 feet high developed 25 seconds after ignition and continued for a further 5 minutes. The residue was irregular in shape and had a swelling ratio of 8 to 10 : 1. After the fierce burning period was ended, the residue still contained unburnt magnesium so that combustion continued for a longer period and disturbance of the residue resulted in the scattering of unburnt magnesium.

*F.M.*7. A fierce flame 4 to 5 feet in height developed 30 seconds after ignition and continued for a further 6 minutes. The flame was slightly less intense than in the case of F.M.1 and there was less unburnt magnesium at the end of the fierce burning period. The residue was more regular and stronger than F.M.1 and gave a swelling ratio of 12 : 1.

The effect of sodium bicarbonate in accelerating combustion and eliminating the production of smoke was most striking. Similar results were shown by sodium carbonate and even by sodium sulphate. The effect is evidently one of catalysis, due to sodium. These additions were equally effective when rubber–kerosine or perspex–benzole were substituted for rubber–petrol; these substitutes also were adequate in all respects.

The mixtures of F.M.1 and F.M.7 were demonstrated (in 10 to 15 gal quantities) at several field trials and gave impressive performances. Both mixtures burnt with an intensely hot flame which made it impossible to approach to within 10 to 15 feet of the burning mixture, and threw off showers of burning magnesium at intervals. Fierce combustion was maintained for 5 minutes after which the rate of burning declined during a further 5 minutes. The thickness of the layer burnt was about 2 inches and the residues in both cases built up to a height of 12 to 15 inches and remained hot for about 15 minutes; they contained unburnt magnesium and burst into flames when disturbed. The mixture containing pitch burnt a little less fiercely but for a rather longer period and left a bulkier residue. It was concluded that the value of the flame obscuration far outweighed that of the obscuration due to the residue and that F.M.1 was the most satisfactory method of obtaining the obscuration required.

Part VI.—The Effect of Various Metallic Sulphides on the Ignition of Magnesium Powder.

It is known that the ignition of certain incendiary mixtures is facilitated by the presence of antimony trisulphide, although this substance itself does not give any sign of violent ignition on being heated in air and its heat of combustion is low (1000 cal per g). The ignition temperature of magnesium depends on its particle size and although the literature values are 540° C in oxygen and just above its melting point (560° C) in air, the value obtained by the method described in this paper for the magnesium powder used in these experiments was just over 500° C in air. No data for antimony trisulphide are available except that it is stated to burn in air below its melting point (550° C). Friedrich [7] found that the oxidation of antimony trisulphide commenced at 290° C for material with a grain size of 0·1 mm or 340° C for a grain size of 0·2 mm.

It was considered that the action of antimony sulphide in improving the ignition of magnesium in mixtures of the two substances was probably due to the fact that at temperatures well below the ignition temperature of magnesium, oxidation of antimony sulphide proceeds at such a rate that the temperature of a mixture of the two materials is rapidly raised to a point above the ignition temperature of magnesium. An investigation was therefore carried out to elucidate this point and in the hope that greater knowledge of the mode of action of antimony trisulphide might lead to improved methods of ignition or to the discovery of substitutes, since the

supply position of antimony sulphide would not have been satisfactory in the event of a demand for larger quantities. Experiments were therefore carried out on the oxidation of antimony trisulphide and later on the oxidation of other metallic sulphides.

Antimony Trisulphide.

The antimony trisulphide was contained in a Pyrex tube 1·5 cm diameter with a central thermocouple pocket, and was heated in an aluminium block electric furnace with a second thermocouple in the aluminium block. The weight of trisulphide used was 5 g with an air current through the tube of 20 to 25 litres per hour. The temperature of the furnace was raised at a

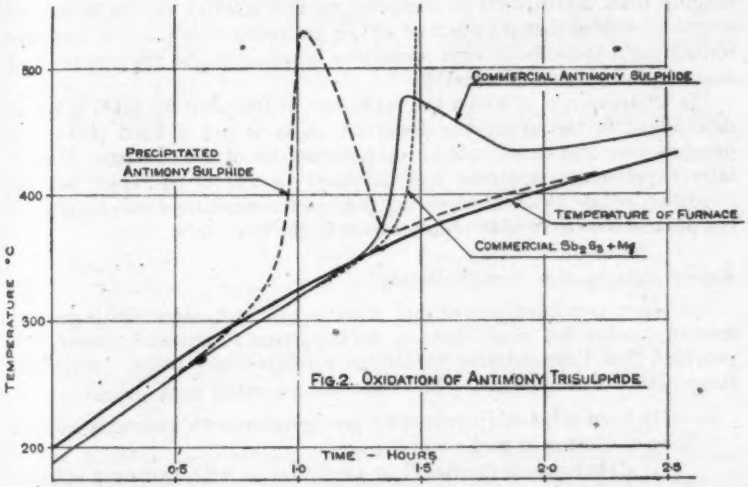

FIG. 2.

rate of approximately 100° C per hour, readings of the temperatures of the aluminium block and the antimony sulphide itself being made at regular intervals.

Two samples of antimony trisulphide were used :—

(*a*) A commercial sample as used in incendiary mixtures (all passing a 72-mesh B.S. sieve). This was presumably the naturally occurring material.

(*b*) A laboratory-prepared sample obtained by precipitation with hydrogen sulphide from a solution of antimony chloride.

The results are shown in Fig. 2. In both cases oxidation (as determined by the evolution of SO_2) began well below 300° C. In the case of the commercial sample a sudden rise of temperature occurred at about 340° C. The precipitated sample behaved similarly except that a sudden temperature rise occurred at 300° C.

In both cases the maximum temperature reached was below the ignition

point of magnesium, but it was almost certain that at localized points considerably higher temperatures were reached. To test this a mixture of 2·5 g of the commercial sample of sulphide and 2·5 g of magnesium powder (grade 5H) was used, and the result is shown in Fig. 2. The rapid temperature rise occurred at a very slightly higher temperature, the difference being presumably due to the dilution of the antimony trisulphide, but the temperature rise was much higher corresponding with the high heat of combustion of magnesium. The stoppers were blown out of both ends of the reaction tube with almost explosive violence.

From these results it was concluded, as suggested earlier, that the action of antimony sulphide in improving the ignition of magnesium is due to the rapid exothermic oxidation of antimony trisulphide at temperatures ranging from 300 to 350° C according to the activity of the sample of sulphide used, so that the effect of adding antimony trisulphide to mixtures containing magnesium is equivalent to a lowering of the ignition point of magnesium by about 150–200° C.

The temperature at which the rapid rise in temperature takes place as determined in the apparatus described above is not a fixed point, but depends *inter alia* on the rate of temperature rise of the furnace. For the later experiments this rate was increased to 200° C per hour and the "ignition point" was taken as the furnace temperature corresponding to the peak of the curve of the temperature in the inner tube.

Experiments on other Metallic Sulphides.

The above results suggested that other metallic sulphides with a positive heat of combustion would have a similar action to antimony trisulphide provided that they oxidized rapidly at a temperature below the ignition temperature of magnesium. The materials examined were :—

(1) *Lead sulphide* (prepared by precipitation with hydrogen sulphide from a solution of lead nitrate).

(2) *Zinc sulphide* (prepared by precipitation with hydrogen sulphide from a solution of zinc nitrate).

(3) *Iron sulphide.* FeS_2.

(*a*) "Coal pyrites." This was a sample of iron pyrites obtained by separation from coal. It contained 39·0 per cent Fe and 36·8 per cent S.

(*b*) A commercial sample of iron pyrites (Fe 38·4 per cent, S 47·8 per cent).

(4) *Cupric Sulphide.*

(*a*) A sample prepared by precipitation with hydrogen sulphide from a solution of copper sulphate.

(*b*) A commercial sample.

Results are given in Table VII together with results for mixtures of the various materials with equal weights of magnesium powder.

The lowest ignition temperature was given by precipitated cupric sulphide (275° C) which, however, failed to ignite the magnesium. The commercial sample of cupric sulphide, which had a much higher bulk density, also had

a much higher ignition temperature (370° C) and effected the ignition of magnesium at that temperature. Lead sulphide gave erratic results, and had a small but definite rise at 350° C with the major peak varying from 450 to 480° C. Zinc sulphide showed no rapid rise in temperature and failed to ignite the magnesium. Iron pyrites (including " coal " pyrites) gave a promising result as although the ignition temperature was higher than that of antimony sulphide there was a rapid rise of temperature at the ignition point, and the mixture with magnesium ignited violently at 420° C (with " coal " pyrites).

TABLE VII.

Experiments with Various Sulphides.

Sulphide.	Calorific value, cal/g.	Ignition temperature, ° C.	Ignition temp of Mg in mixture with sulphide, ° C.
(1) Antimony trisulphide (comml)	1000	350	360
(2) Lead sulphide	650	450–480	no ignition below 490
(3) Iron sulphide	500	—	—
(*a*) Coal pyrites	—	410	420
(*b*) Commercial iron pyrites	—	440	*ca.* 430
(4) Cupric sulphide	240	—	—
(*a*) Precipitated	—	255	no ignition below 490
(*b*) Commercial	—	375	370
(5) Zinc sulphide	400	—	no ignition below 490
(6) Cupric sulphide (pptd) and coal pyrites	—	275	275
(7) Cupric sulphide (pptd) and commercial iron pyrites	—	275	275
(8) Lead sulphide and coal pyrites	—	405	420

The mixture of precipitated cupric sulphide and iron pyrites gave a particularly interesting result. The cupric sulphide, which had an ignition temperature of 275° C, failed to ignite magnesium, but a mixture of cupric sulphide and iron pyrites gave a single temperature peak at 275° C with a much higher rise in temperature (up to 670° C) than that given by copper sulphide alone, showing that the cupric sulphide had ignited the iron sulphide at 275° C instead of its normal ignition temperature of 410° C. Furthermore, a mixture of iron pyrites and cupric sulphide ignited magnesium at 275° C so that the ignition temperature of magnesium was lowered by over 200° C. A mixture of lead sulphide and iron pyrites, on the other hand, showed no major temperature rise until the ignition temperature of the iron pyrites was reached, the minor peak at 350° C for lead sulphide having no effect on the ignition of iron pyrites.

From the results of this investigation it was possible to suggest the following substitutes for antimony trisulphide in incendiary mixtures, in the following probable order of efficiency :—

(1) Mixture of copper sulphide (pptd) and iron pyrites.
(2) Commercial copper sulphide.
(3) Iron pyrites.

Although, in practical trials the first of these proved to be highly suitable, it was found that iron pyrites, which was much easier to obtain in the quantity desired, was a satisfactory substitute for antimony trisulphide, and was therefore adopted for large-scale work, using the material obtained by separation from coal (" coal pyrites ").

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Fuel Research Station,
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London, S.E.10.

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THE OIL SHALE DEPOSITS OF THE WORLD AND RECENT DEVELOPMENTS IN THEIR EXPLOITATION AND UTILIZATION, REVIEWED TO MAY 1947.*

By W. H. CADMAN, M.B.E. (Fellow).

SUMMARY.

In this paper a brief survey is given of the oil-shale deposits in various countries, including some of the war-time and more recent developments in Great Britain, France, Estonia, Sweden, Spain and Portugal, Italy, Czechoslovakia, U.S.S.R., Turkey, Bulgaria, Germany, Japan, Australia, New Zealand, Canada, South Africa, India and Burma, Brazil, and the United States of America.

A general description is given of the nature and chemical composition of the oil shales and some oil shale products.

No attempt is made to include any detailed information. This is left for the Second International Conference devoted solely to this subject, to be convened in the future by the Institute of Petroleum (London).

The enormous oil-shale deposits in the world primarily form a potential raw material for the production of oil. The paper indicates to what extent the exploitation of these potential oil reserves has been carried out, and also to what extent an economical method of obtaining oil from shale has been developed, or is under development.

The subject discussed is closely related to national self-sufficiency in case of future emergency in countries without indigenous oil supplies. It suggests a means of contributing to the increasing demands for liquid fuels, whilst the world's supplies of petroleum are inevitably diminishing rapidly, and it may be of great importance as a potential source of oil when the oilfields of the world are ultimately exhausted. Reference is made to the Swedish discovery of uranium in oil shale and spent shale, and to the great value of shale uranium as a source of atomic energy.

INTRODUCTION.

ATTENTION has lately been focused on the world resources of oil and coal, and on other sources of power-producing fuel.

As regards petroleum and coal, the world's reserves are rapidly being used up, and will undoubtedly eventually become economically unworkable —oil first and then coal—in each case due to the present rapid rate of consumption. Whilst the day is still far distant when supplies of oil and coal begin to approach exhaustion, the fact remains that the world's reserves of both these fuels are limited, and will inevitably fail within a measurable period of time.

The production of oil from shale and possibly also of atomic energy from shale uranium will undoubtedly, with the help of the chemists, play an important part in the future as a source of fuel and power.

Although the known deposits of oil shale are numerous, comparatively few seams are economically workable at present. Either their yield of oil is too low or the costs of mining, retorting, and refining are too high.

At the present time far more attention is being paid to the study of shale oil production in America than in any other part of the world, but the time

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is not far distant when it may be necessary to augment the supply of motor fuel and lubricating oils in the United States from her natural resources by other potential sources of supply, including the oils obtainable from her indigenous oil shales. This interest in oil shale exploitation in the world's greatest oil-producing country is regarded as being highly significant.

Definition of Oil Shale. Nomenclature.

Oil Shale is generally defined as a compact rock having a stratified or laminated structure. The deposits are believed to have been formed by the sedimentation of clay, mud, silt, and organic matter which, owing to subsequent changes, yield oil when distilled, and leave behind ash, or spent shale, usually amounting to over 33 per cent by weight.

Torbanite is a material intermediate between shale and coal. It differs from coal in containing more hydrogen and producing hydrocarbons, when subjected to destructive distillation, which mainly belong to the paraffin and olefin series, as distinct from those of the benzene series obtained from coal. It differs from oil shale in giving a higher yield of oil on retorting, yields of over 160 gal per ton being recorded. It is now generally accepted that a torbanite differs from a coal so markedly that it must be regarded as a distinct class of mineral.

The Torbanehill mineral, from which the name is derived, was the material originally distilled for oil at Bathgate in Scotland. It yielded up to 120 gal per ton. Rich torbanite also occurs in France, New South Wales, South Africa, and Eastern United States.

G. W. Lepper has drawn attention to the fact that, whilst from the point of view of the technical chemist concerned with oil production there might be an almost imperceptible gradation in his raw material from poor oil shale through richer oil shale to lean cannels, richer cannels and, finally, to torbanite, to the geologist oil-shales and cannels are lithographically distinct.

The term *kerogen* is a convenient name for the organic matter from which oil is produced when the deposits containing it are heated. The industrial application of oil shale based on the thermal decomposition of this contained organic matter has been extensively studied.

So far, however, comparatively little work has been done on the chemistry of kerogen, and its chemical constitution still remains to be thoroughly investigated. Recent work at the Imperial College of Science and Technology by Down and Himus has thrown some light on the solution to this problem. They have produced evidence of a benzenoid structure in the constituents of some kerogens, but other kerogens, notably those of Estonian shale, show no evidence of benzenoid structure.

These two investigators have also suggested a classification of oil shales and cannel coals, based entirely on the nature of the plant remains and on the nature of the mineral matter present where that is important, prefixing the names by an adjective explanatory of the locality from which the material was obtained.

It is hoped that the controversial question of precise classification and nomenclature of the whole range of oil-yielding rocks will be authoritatively settled and internationally used before long. They are outside the scope of this paper, in which the term *oil shale* includes what are commonly known as torbanite and shales which yield oil on retorting.

Nature and Origin of Oil Shale.

The general consensus of geological opinion points to the shale beds having been laid down at the bottoms of quiet lakes and lagoons containing large quantities of nearly fresh water. This oil-yielding material was named "kerogen" by Professor A. Crum Brown from two Greek words meaning "producer of wax." It is formed from low forms of plant life, such as algæ, pollen, and spores and spore coats. These plant remains have been identified in microphotographs. Besides being generally regarded as of vegetable origin, there is also a theory that, in part at least, it may be of animal origin resulting from the insects and larvæ and fish in the sediments.

Oil shale being a sedimentary rock has a fine grained or laminar structure. It varies in colour from grey to brown, blue, or almost black. Thin pieces of oil-rich shale can be cut from a lump with a knife and can be lighted with a match, when it burns with a sooty flame, and with a smell similar to petroleum.

Crude shale oil can only be produced by the destructive distillation by heat of the kerogen content of the shale.

The chemical composition of the kerogen varies greatly in different oil shales. It is not a simple hydrocarbon, but consists for the most part of large and very complex molecules. Chemists are not agreed as to its structural formula.

In addition to hydrogen and carbon, kerogen also contains some oxygen, nitrogen, and sulphur. The nitrogen can be easily recovered on distillation as ammonia, at one time a valuable by-product. Sulphur removal is more difficult and involves costly refining.

The inorganic material in oil shale or residue after distillation is largely composed of complex silicates consisting mostly of alumina and ferric oxide and lime. This inorganic material, much of which is structureless, forms by far the largest proportion of the shale and constitutes the spent shale remaining after the oil has been recovered. For many years the residue was regarded as a waste material, and it is only comparatively recently that it has been found useful for brick- and cement-making. From some shales the mineral residues retain most of the fixed carbon in a very finely divided and reactive form. Since this carbon is readily combustible, it can be utilized as a fuel provided the carbon content is more than about 6 per cent.

Martin J. Gavin has shown that there is apparently a definite relationship between the percentage of nitrogen in oil shales and their oil yield in gal per ton. This relationship probably holds because the nitrogen exists in the shale combined with the kerogen or oil-yielding constituent.

The nitrogen content of the different oil shales varies from a trace to more than 1 per cent. In the Scottish oil shale and the Eastern shales of the U.S.A. the nitrogen content appears to vary inversely as the oil-yielding possibilities, but in the oil shales of the Western part of the United States the reverse seems to be the case.

The sulphur in the different oil shales varies from none or a mere trace, to more than 6 per cent. Some of the sulphur exists in shale combined with the organic matter, yielding sulphur compounds which largely account for the objectionable colour and smell of the oils produced from sulphurous

shales. Most of the sulphur, however, is in the form of iron sulphides and gypsum. Practically all oil shales containing sulphur produce gaseous hydrogen sulphide when retorted.

Dorset shales are high in sulphur compounds (up to 7 per cent S) and when distilled the shale oils produced are also very sulphurous (about 6 per cent S).

Some oil shales are found to contain phosphates and small quantities of potash, but the amount present is insufficient to make their recovery a commerical proposition.

Aluminium is frequently present in considerable quantity, for example in New South Wales torbanite (64 per cent Al_2O_3) and in the alum shales of Sweden.

The rare metals, gold, silver and platinum, have been reported as occurring in some oil shales, but an investigation made by the U.S. Bureau of Mines in 1922 concluded that oil shale would never be a commercial source of gold, silver, platinum, or allied precious metals. Traces of arsenic have been found in Scottish oil shale equal to 0·00056 per cent by weight calculated as As_2O_3.

At the time of the above investigation the element-uranium was not in the limelight, and the possibility of its existence in oil shale appears to have been overlooked. This is remarkable because it is now known that the presence of uranium in shale deposits in Sweden was first demonstrated by A. E. Nordenskiöld in 1894.

It is also now known that in the aggregate large amounts of uranium are contained in the oil shale deposits in Sweden, and that some shales are also rich in vanadium, up to 0·4 per cent by weight. Josef Eklund, of the Geological Survey of Sweden, in a recent note on uranium, published in the *Skandinaviska Banken Aktiebolag* Quarterly Review, calls attention to the discovery of shale uranium, and mentions that shales of similar origin are already known in the U.S.A., U.S.S.R., Norway, Denmark, Czechoslovakia, Germany, Belgium, and France, besides Sweden, and that it is possible that they can be found in practically all countries. If atomic energy is to play an important part in the world's peace-time production of power, as most scientists believe, there must obviously be sufficient raw material available from which it can be produced at a reasonable price. Eklund says that in Sweden alone the already mined deposits, with 0·1 to 1 per cent uranium content, are estimated to contain 50,000 tons of uranium, all of which deposits have previously been mined for radium, and the quantity of uranium in shale, largely oil shales, of 0·02 per cent U content, amounts to 1 million tons; the deposits in the U.S.A. and Soviet Russia are the same size. If it is possible to utilize uranium shale of poorer quality the potential supplies increase rapidly.

He concludes by saying: "In a time of great need, atomic energy, which has already made history, is being developed by a research unparalleled in history. It will be found that nearly every country has played a part in its origin and development, and Sweden's particular contribution may be to develop this source of raw material for atomic energy."

Mining and Retorting of Oil Shales and Refining of Shale Oils.

The technique of mining shale in different countries and of refining shale oil to obtain marketable products is outside the scope of this paper. Shale mining in some areas is analagous to coal mining, and shale oil refining to petroleum refining.

As regards the retorting of oil shales, briefly this process usually consists in heating the shale, previously broken into small pieces, in specially constructed retorts, with air and steam injection, when it yields oil vapours, combustible gases, and ammonia, the amount of which depends upon the nitrogen content. From the vapours crude shale oil is easily condensed and the ammonia, if any, recovered in the ammoniacal water. By means of oil absorption or activated carbon, the light motor spirit fraction carried over with the uncondensed gases can be recovered.

At the temperature reached in the retort, the large complex kerogen molecules are decomposed, probably first into bitumen which is then cracked into smaller and simpler molecules of gaseous, liquid, and solid hydrocarbons which resemble petroleum in many respects.

At the end of the distilling operation, about two-thirds of the nitrogen content of the shale is recovered in the ammoniacal water, and there remains behind in the retort only the spent shale, or the mineral matter and fixed carbon.

Some oil-shales tend to soften and to cake at about 450° C and their softening points vary with the oil content of the shale. This characteristic must always be taken into account when deciding upon the most suitable type of retort to be used for handling any particular kind of oil shale.

If the retorting of the shale is carried out in the presence of steam it is found that the distillation is more rapid, and the yield of oil appreciably larger than without steam, whilst in some cases the oil contains a larger proportion of high-boiling constituents. Excluding the spirit recovered from the retort gases, the crude oil is composed of C — 85–83 per cent; H_2 — 12·64 per cent; N — 0·74 per cent; S — 0·46 per cent; and O_2 by diff 0·33 per cent.

Like petroleum, shale oil can be cracked to increase the yield of the low boiling-point fractions, and is amenable to hydrogenation. It can also be used as a raw material for the manufacture of detergents and other chemicals.

In the following survey all the known oil shales of any importance have been included, so far as information is available.

Great Britain.

Scotland. The Scottish shale fields extend in a south-westerly direction for a distance of about 15 miles, from below the Firth of Forth in Mid-Lothian into the county of West Lothian. The area included in the seams of richest oil content covers about 75 square miles in Central Scotland.

These deposits have been mined for the production of shale oil since 1851, when the Scottish oil shale industry was founded by a Glasgow chemist, Dr James Young, F.R.S. (1811–1883). Young took out his first patent for the extraction of oil from coal in 1850, 8 years before Drake sank the first

American petroleum oil well in Pennsylvania, which profoundly modified the future development of the shale oil industry.

It was known before 1850 that oil could be obtained by distilling coals and shales, and British patents were taken out for such processes dating from the seventeenth century.

At the 1851 Exhibition there were exhibits of oils and other products from the shales of France and Germany, and before the establishment of the Bathgate Works by Young in 1853 several attempts had been made to obtain oil by distilling the Kimmeridge shale of Dorset.

It is in the Lothians of Scotland that the British oil shale deposits have been exploited and developed to the greatest extent, and are still being retorted by the Scottish oil shale industry.

The oil shale beds in Scotland occur in the Calciferous Sandstone Series of the Lower Carboniferous lying between the old Red Sandstone and Carboniferous Limestone. The series in this locality are about 5000 feet thick, with recurring outcrops, which results in large areas of oil shale being brought to within easy mining depths.

As found Scottish oil shale is free from any smell of oil or gas. It contains no grit and can be cut with a sharp penknife into shavings which curl up like those from a pencil.

The beds of shale range in thickness from a few inches to about 15 feet, the workable seams being from 4 to 12 feet thick. Fossils are scarce, but remains of Carboniferous flora and also of fish have been found.

The oil shale differs in quality with the different seams in which it occurs, and the yield of crude oil varies from 16 to 40 gal per ton. It contains about 2 per cent by weight of sulphur. For a long time only shale yielding 25 gals or more per ton was fed to the retorts, but now shale averaging 22 gals (16 to 30) per ton is in use. On treatment this crude oil yields motor spirit, kerosine, gas oil, diesel oil, light lubricating oil, paraffin wax, fuel oil, and coke. It is particularly suitable for diesel oil, the yield being as high as 50 per cent by volume.

The ammonia is converted into ammonium sulphate, amounting to about 30 lb per ton of shale. The gas from which scrubber naphtha is first removed is slightly more than sufficient to satisfy the heat requirements of the retorting operations.

The present rate of production, 1946, of Scottish oil shale, is about $1\frac{1}{2}$ million tons per annum from twelve mines and from open-cast workings.

Satisfactory bricks are now made from spent shale by mixing it with lime, moulding, and subjecting to steam in autoclaves at 150 to 160 p.s.i. pressure.

The estimated reserves of Scottish oil-shale vary from 480 to 884 million tons.

Dorset and Norfolk. Extensive deposits of highly sulphurous bituminous shales of Jurassic age are located in Dorset and Norfolk. They are typified by that found at Kimmeridge near the Dorset coast which, although yielding from 40 to 70 gal of crude oil per ton, have not been commercially exploited so far, due to the prohibitive cost of removing the sulphur from the shale oil, which averages about 6 per cent by weight. Parts of the seams are so rich in organic matter that they have been used locally as solid fuel for centuries.

Other oil shale deposits have been found elsewhere in the British Isles, but only in small quantities.

France.

The French bituminous shale industry is more than 100 years old.

The richest deposits occur in Central France at Autun (Saône-et-Loire) and at St. Hilaire (Allier) in the basin of Aumance. Low grade oil-bearing deposits are found in the South at Lavernhe and Séveràc-le-Chateau, and also in the east at Creveney where they are very extensive but undeveloped. This low-grade shale only awaits an efficient distillation process to enable it to be retorted economically on a large scale.

At *Autun*, the shale occurs in the Permian formation at about 325 feet below the surface with an average seam thickness of 6 feet (3¼ to 11). The deposit is extensive covering about 80 square miles.

So far distillation has been carried out in Pumpherston retorts distilling 840 tons of shale per day when all retorts are operating, as in Scotland; but these Scotch retorts are being replaced gradually by a new type called the Lantz retort, developed at St. Hilaire, Aumance, which has proved to be more suitable for retorting this kind of shale.

Autun shale yields 6 to 7 per cent by weight of oil by the Fischer assay, and 85 per cent of that yield in plant operation. It contains about 2 per cent by weight of total sulphur.

The French shale reserves are estimated to be about 70 million tons in the Autun area alone.

At *St. Hilaire* the seam is also Permian and alternates with workable coal seams. The shale worked is about 6 feet thick, and the present output is about 500 tons daily.

A pilot plant of unique design has been in operation since 1938 treating about 80 tons of oil shale daily and yielding about 16½ gal of oil per ton, which is nearly 100 per cent of the Fischer assay.

Recently two large-scale retorts, called "G.P," based on the pilot plant have been installed, with a throughput of 1000 tons of shale per day.

The reserves of the St. Hilare region are estimated at 30 million tons.

The shale fields at *Lavernhe and Séveràc-lè-Chateau* are about 2 miles apart, and the shale is of Toarcian age, stated to be comparable with the English Kimmeridge oil shales. The thickness of the seam varies from 32 to 50 feet.

The total reserves of the Séveràc-le-Chateau deposits are unknown, but the outcrops indicate from 500 to 1000 million tons.

Much the largest oil shale field in France, judged by the outcrops at present known, is of Lower Toarcian age at Creveney about 90 miles south-west of Strasbourg. The thickness of the shale beds varies from 30 to 50 feet, and the oil yield is said to average less than 11 gal of oil per ton, so that it must be considered of low grade. The possibility of distilling this shale *in situ* by underground methods is now under consideration.

The reserves are estimated at 2000 to 3000 million tons, and the recoverable oil at 18,000 to 36,000 million imp. gal.

Other oil shale deposits are located in the Cretaceous at Vagnas in the Ardèche, in the Oligocene at Bois d'Asson (Basses-Alpes), in the Carboniferous at Bozon (Var), and Faymoreau (Vendée).

Estonia.

In north-east Estonia an oil-bearing shale known as "Kukersite" was discovered about 150 years ago. The dry rich shale can be ignited easily with a match, and it was first exploited as a fuel being used as a substitute for coal. The production of oil from this material dates from 1919, after the first World War, but for some time about one-third of the total shale mined was used for fuel on the railways and in stationary and power plants.

Kukersite is of Lower Silurian age.

Outcrops of the Estonian oil shale beds have been traced for over 70 miles running parallel with the southern shore of the Gulf of Finland, between Tallinn in Estonia and as far as Leningrad in the U.S.S.R.

There are important shale workings at Kohtla-Järve, Kiviõli, south of Sillamagi, and at Eumoisa.

The yield of oil on retorting varies from 48 to 86 gal per ton.

The retorting of Estonian oil shale is difficult because of the formation of asphalt at about 300° C, which causes lumps of shale to stick together and block up the retort. For this reason specially designed retorts have been found necessary.

The quantity of oil shale excavated increased from practically nothing in 1918, by about 40,000 tons a year, to 750,000 tons in 1936. From 1936 to 1939 it increased by about 300,000 tons a year to 1,700,000 tons, as a result of the German efforts to obtain oil from this source.

The oil shale reserves in Estonia were estimated to be 5000 million tons (5 milliards) before the second world war, of which 3½ milliard tons were considered as technically workable and capable of producing 700 million tons of oil. An estimate of the shale oil reserves made before the German invasion in Estonia gave about 30,000 million gal, based on 20 to 30 per cent by weight of the shale being convertible into crude oil.

During their 2 years of occupation before the successful German invasion of Estonia in 1941, the Russians planned to increase the production of shale oil by five times in 5 years. With the German occupation of Estonia from 1941 to 1944 a target of 1,653,000 tons of oil per year was set as the shale oil production figure from the Estonian deposits. The construction of new shale oil plants to obtain this increased production was almost completed when the Russians again overran Estonia in September 1944.

It is stated that three new refineries are now under construction which are to be connected to Leningrad by pipeline in order to supply that city with gas from the Estonian oil shale works.

In addition to shale oil and gas, the U.S.S.R. also plans to develop the Estonian shale oil industry by 1948 in such a way as to give raw materials for the production of chemicals, plastics, and sulphur.

Sweden.

Sweden has extensive deposits of oil shale, of which the largest and richest are found in Kinne-Kleva at Kinnekulle, and at Yxhult in the Province of Närke.

The shale belongs to the Cambrian–Silurian series. The seams are frequently 30 feet thick, and can be mined cheaply in open cuts.

The oil content of Närke shale averages only from 5 to 6 per cent, or 12 gal per ton of shale. The recoverable gas and sulphur is also about 5 to 6 per cent by weight of the shale. It is estimated that the open pit resources of this shale are very extensive and amount to about 1000 million tons. The total reserves of all the oil shale in Sweden have been stated to be about 5000 million tons located in situations convenient for rail and water transport.

Large reserves of alum shales occur in south-east Skane and other parts of Sweden, yielding about 2 per cent by weight of oil only, which is too low for the economic production of oil by distillation. This shale, however, is rich in vanadium and aluminium, so that the extraction of these metals by chemical methods, with oil as a by-product, may render them economically workable. They are at present extensively used for their fuel value in lime burning and for making insulating building bricks, etc.

By 1942 the production of shale oil in Sweden was estimated to have reached 9½ million gal, and about double that quantity in 1943. Since then the production capacity has been increased, and last year, 1946, there were no less than four different processes in operation in Sweden for the production of oil from shale on a commercial scale. About 4000 tons of shale are at present mined per day at Kvarntorp.

The Närke deposits at Kvarntorp are richer than the Kinne-Kleva oil shales and are estimated to yield a total of from 12,000 to 15,000 million imp. gal of oil. As these shale deposits are found deeper down from the surface than those at Kinne-Kleva the mining costs by standard methods are higher, thereby increasing the cost of producing shale oil from this source.

In order to overcome this, Dr Fredrik Ljungström invented a new process for the extraction of the shale oil without incurring any mining costs. This revolutionary process involves the electrical heating of shale underground *in situ* from bore holes without mining it.

An experimental plant to try out the process was first installed at Ekeby, and was partly financed by the State. Up to January 1945 16,000 tons of shale oil had been produced at the rate of 3 tons an hour. To-day a third of the oil production in Kvarntorp (where about 4000 tons of shale are also mined daily for retorting) comes from the Ljungström process.

This process is now being operated by a Swedish shale oil company, which is financed by the Government. The shale bed at Kvarntorp is 50 feet thick and has an overburden of about 10 feet.

Holes of from 1½ to 2 inches diam for the electrical heating elements are drilled into the shale at the points of a hexagon, the distance between each of the six holes being approximately 8 feet. In the centre of each hexagonal set-up another hole is drilled for the vapour line. Two hundred and fifty of these hexagonal set-ups are constructed and interconnected for the supply of electrical energy for distilling the oil from the shale. All the vapour lines from the centres of the hexagons pass through a common header which carries the oil vapours to a central condensing plant. The heating of the shale is not done by hydro-electric power, but it has been found to be cheaper to produce it by making use of the combustible material remaining in the spent shale of the Berg retorts operating nearby. Le Mont waste heat boiler tubes for steam generation are inserted in the hot spent shale.

After being used to generate the cheap electrical energy required the spent shale is utilized for brick-making and for the production of alumina and potash. From the gases produced at the shale oil distillation plant, ethylene and propylene are obtained for the manufacture of chemicals. The propane and butane are sold as bottled gas.

It requires 3 months to heat up the shale before vapours begin to come off, after which the area concerned remains on make for at least 2 months. Many months are required for the formation to cool down afterwards, and the warm soil is made use of for growing vegetables.

Whilst this process avoids the two principal and most expensive operations of the older methods of oil production from shale, viz., mining and retorting, in order to be economical it depends entirely on a cheap source of electrical energy for the underground heating. The possibilities of successful application of this process in other countries will also depend upon the yield of oil obtainable from the shale available and also on the geological formation of the oil shale.

Egloff reports that in this method of shale distillation a ground temperature of 100° F is created by the electrical heaters used to force the vaporized oil out of the shale. He found that the Swedes were making use of this tropically heated soil for growing more and larger vegetables. For example, he describes tomatoes three or four time the normal size.

Another method now used in Sweden to produce oil from these low-grade shales is that invented by Sven V. Bergh. The crushed shale is retorted with the addition of steam in a large number of small cast iron retorts grouped into a furnace, using the heat from the surface combustion of the shale coke for the low temperature distillation.

There are also three other methods in commercial use in Sweden for retorting shale.

Some of the black pyritic oil shale deposits in the central Swedish provinces have recently been found to contain appreciable quantities of uranium, amounting to a million tons in shale of 0·02 per cent U. The already mined deposits with 0·1 to 1 per cent uranium content are estimated to contain about 50,000 tons of uranium. This important discovery of extractable shale uranium makes Sweden the third richest country in the world as a potential source of uranium—a matter of considerable interest as a source of atomic energy.

Egloff has referred to uranium oxide recoverable as one of several by-products remaining in the oil-exhausted shale, which he said contained 200 grammes of the radio-active compound per ton. He estimated that Sweden's oil shale deposits contain about 500 million pounds of uranium oxide. Although his figure is smaller than that given by Eklund, it is nevertheless a very considerable amount. Some oil shales in Sweden are high in vanadium, up to 0·4 per cent V.

Spain and Portugal.

Spain. Deposits have been found in the Pedro Martinez Basin, with a seam thickness of from a few inches to abut 9 feet.

Other oil-shale beds occur in Granada, at Rubielos de Mora (Castellon)

and at Mora (Teruel). They are of Cainozoic age. In samples of Castellon shale, Conacher found well preserved insect remains.

A large-scale shale oil distillation plant was under construction in 1946. The Puerto Llano shale to be used yields on assay about 27 gal of crude oil and 22 lb of ammonium sulphate per ton.

The carboniferous deposits in Spain have been estimated to contain about 10 million cubic metres of shale, with an average yield of 12 per cent of oil by weight. They are associated with workable coal seams.

Portugal. True oil shales in the Lower Lias have been found in Portugal, outcropping at Peniche, S. Pedro de Muel, and Quiaios. The seams are thin and unlikely to yield any appreciable oil supplies.

Italy and Sicily.

Italy. In the Alps in Northern Italy at Besano, south of Lake Lugano, numerous beds of bituminous shales occur in the Alpine Trias, from which a small quantity of oil varying from 10 to 30 per cent by weight, known locally as " Ichthyol " or fish oil, has been distilled. This shale oil has a sulphur content of 4 to 11 per cent by weight, mostly in the form of thiophene derivatives. At Melide and at Seefeld these shales are worked and the oil is used for pharmaceutical preparations. These Trias shales extend into Switzerland near Melide, and similar shales occur in the Upper Trias in the Austrian Tyrol.

Bituminous shales, from which a good asphalt can be made, have also been located in the Cretaceous near Morraro in the Trentino.

Sicily. Bituminous shales of considerable thickness have been reported from many districts in Sicily which are believed to be of Eocene age. They contain from 9 to 19 per cent by weight of hydrocarbons. It is stated that distillation tests have met with good success.

Thin bituminous shales, yielding up to 10 per cent oil, have also been found in the Messina district in the Lower Miocene.

Czechoslovakia.

A deposit of bituminous shale located in the Kladno coal-basin in Bohemia covers an area of about 25 square miles. The seams are Permian and are from 2 to 4 inches thick. The shale is mined together with the underlying seam of poor quality coal, and used as a high calorific value fuel in glass works and for gas making. It has never been retorted commercially for oil production, although tests have shown that freshly mined Kounova shale yields 18 to 20 per cent of oil by weight. The crude oil contains about 10 per cent by weight of phenols.

Extensive Middle Miocene beds of Cypris oil shale have been known for some time in Western Bohemia between Falknov and Cheb. Unlike the other shale deposits in Czechoslovakia this shale has never been used as fuel, nor for the production of oil.

U.S.S.R.

The principal oil shale deposits in the U.S.S.R. are along the Volga and in Leningrad Oblast, whilst others are known at Kuibyshev, Saratov, Gorki Provinces, and in the Khuvash and Tatar autonomous republics.

Samples of Russian bituminous shales from the Manturov deposit in the Gorki area gave 12·9 per cent of crude shale oil, whilst the Romanov shale yielded 14·1 per cent of crude shale oil when tested in 1946. The yield of finished re-run gasoline obtained from a typical U.S.S.R. shale by a special "thermal solvent extraction" process was 15·5 per cent. The method consists in heating the shale to about 400° C at 30 atm pressure, using a solvent such an anthracene oil, petroleum diesel or fuel oil, various shale oils or hydrogenated shale oils, converting, it is claimed, up to 95 per cent of the shale organic matter into liquid fuel.

Under these conditions it is considered that catalytic cracking may occur, the alumino-silicates in the shale acting as the catalyst. The best solvent reported is a fraction of shale oil with b.p. 220 to 370° C.

Little progress had been made in the commercial development of Russian oil shale deposits up to 1928, but in 1938 production had increased to 562,100 metric tons with a target of 4 million tons for 1942.

In 1944 the oil shale reserves in the Soviet Union were estimated to be 55,000 million metric tons.

When the Russians occupied Estonia during the Second World War the German had just completed their greatly enlarged shale oil installations to treat Estonian shale. Under the Russian occupation these plants are doubtless now in full operation, although it is quite possible that the best of them have already been removed to the U.S.S.R.

Turkey.

Important deposits of oil shale were discovered some time ago near Ankara, and also in the north-western and western regions of Turkey.

In the district of Bolu, south-west of the well known Eregli coal area on the Black Sea coast, the shale deposit discovered was said to total about 7 million metric tons, whilst in the district of Izmit, opposite Istanbul, reserves aggregating 30 million tons have been estimated, with an average oil content of 2 per cent.

In addition extended reserves totalling 15 million tons, with an average yield of 11 per cent of oil, have been located in the shale deposits discovered near Manisa, to the north-east of Izmir.

Bulgaria.

Deposits of oil shale yielding from 18 to 55 gal. of oil per ton have been located in Bulgaria, near Breznik, some 8 miles to the north-west of Pernik, the Bulgarian coal-mining centre, and about 30 miles to the south-west of Sofia. Nothing is yet known as to the extent of these deposits nor of the field.

The Ministry of Commerce has been studying the most appropriate method of producing gasoline from this oil shale, but no commercial exploitation of Bulgarian oil shales has yet been reported.

Germany.

Large deposits of low-grade oil shale have been located in Germany, particularly in Württemberg, and others are known in Messel, Hesse,

Bavaria, Baden, and the Rhine Provinces. The Württemberg shale seams lie in the Upper Lias formation, being interspersed with limestone. They vary in thickness from 28 to 70 feet, with an overburden of impervious clay, which is said to be absolutely necessary for the distillation of the shale *in situ*.

Little or no encouragement was given to investigators in the field of German oil shale retorting up to the Second World War, but with supplies of petroleum diminishing, the Germans were forced to develop with all possible speed their own low-grade oil shale deposits, especially those near Balingen in Württemberg.

A retorting plant was installed at Frommern, Württemberg, to treat 1100 tons of shale and to yield about 40 tons of oil daily. The average yield of oil is 4·5 per cent by weight (Fischer assay).

The Germans developed some novel processes for treating oil shale, three of which may be briefly mentioned :—

(1) *Meier Grolman, or Otto Retort.* The shale, after having been crushed and screened to a size of 0·2 to 2 inches, is fed to the vertical retort, two sides of which consist of louvres. Each retort has a daily shale throughput of 200 tons. The yield of oil per ton of shale is about 3·4 per cent by weight, or 8 gal per long ton.

The spent shale is about 80 per cent of the raw shale. Its high lime content (28 per cent CaO) solved the problem of its disposal.

It is used in cement manufacture, which in this case has become the primary product, with the shale oil as a by-product. It is stated that shale cement is very little inferior to Portland cement.

(2) *Distillation of Shale in Situ.* The underground pyrolysis of shale in Germany is effected by internal combustion methods, which are quite distinct from the earlier Ljungström or Swedish underground methods of distillation by electric heating. The German technique is based on the Russian underground process for the gasification of coal *in situ*.

At Württemberg the oil is recovered by heating the shale in a number of parallel underground chambers, each 200 feet long by 6 feet 6 inches wide by 7 feet 3 inches high, which are first prepared by ordinary mining methods. In order to construct these chambers two main roads are first driven 425 feet apart into the hillside containing the shale deposits, and then connecting roads are made between them 200 feet apart. All the shale excavated in making the roads and chambers is removed to the surface in wagons for subsequent retorting there. Explosive charges are then inserted in the side walls and roofs of each chamber, and fired to produce a mass of loose broken shale by the blasting, which fills the chambers. Each chamber is then bricked up at the ends, an air intake pipe with valve being inserted at one end and an offtake pipe connected to a section main in the other end. The suction is obtained by an electrically driven exhauster. Before sealing, the shale is set on fire by burning some coke and wood. The rate of combustion is controlled by the air intake valve.

As the shale becomes heated in the chambers the distillation products are drawn off by the suction fan. About 80 per cent of the

heavy shale oil condenses in the outlet pipes from the chambers and in the 24 inch main, from which it is drained for collecting. The remainder of the oil (20 per cent) is condensed above ground in a standard condensing system. So far no attempt has been made to strip the light hydrocarbons from the uncondensed gases, which are blown to the atmosphere. The volume of gas produced by a ton of shale is about 20,000 cu. ft, containing from 1 to 2 gal of motor spirit per ton. The time taken to distil six chambers in parallel is from 16 to 20 days.

So far the yield of oil obtained is very low, averaging only 800 gal daily from 220 tons of shale distilled in this way. This is equivalent to 1·5 per cent by weight of the shale treated, or only 33 per cent of the Fischer assay.

More experimental and development work needs to be done on this interesting process before it can be considered to be a commercial success. For the distillation of large deposits of low grade shale *in situ* this process has definite possibilities.

(3) *Meiler Process.* This process, which is operated in the Balingen district, near Dotternhausen, resembles that employed in carbonizing wood for charcoal manufacture.

The broken shale is built into large piles on the top of a series of suction pipes. The shale quarried in the neighbourhood by mechanical diggers is first broken in hammer mills and screened. Each pile is about 125 feet long by 10 feet deep by 40 feet wide, and contains about 1500 tons of shale.

A fire of peat, coal, or wood is first kindled on top of the pile, and gaseous products of distillation are removed as generated by an exhauster to a cooling system to condense the liquid products.

The quantity of oil recovered by this process is said to be 80 per cent of that obtained by the Fischer assay.

The time taken to distil each pile is from 2 to 3 days.

Japan.

No oil shale appears to have been found so far in Japan. There are, however, extensive deposits and oil shale retorting plants in Manchuria.

The shale is of poor quality, but because it has to be removed in any case in order to get at the valuable coal deposits which lie below, it is possible to make use of it commercially.

The Manchurian shale field comprises an area of about 11 square miles. The seams are about 450 feet thick, and the average yield of oil is 5·5 per cent by weight.

The reserves of oil shale were estimated in 1938 to be 540 million tons.

The quantity of shale oil produced was about 1 million brl in 1939. By 1945 the annual production had increased to more than 3½ million brl.

The American Technical Investigation Teams sent to Japan after the war found that the output of shale oil at Fushun exceeded, up to 1944, the combined output from all the Japanese synthetic oil plants, 55 per cent of the oil from which was produced in Manchuria and not in Japan.

Captured documents belonging to the South Manchurian Railway,

which operated the shale oil plants at Fushun, showed that they aimed at increasing the total production of their two shale oil plants to 850,000 tons per annum by 1948.

Australia, Tasmania, and New Zealand.

Australia. Rich and extensive oil shale or torbanite deposits occur in the Upper Coal Measures between the Triassic Hawkesbury Sandstones and the Permo-Carboniferous strata, in the Wolgan and Newnes–Capertee Valleys of New South Wales. The seams vary in thickness from a few inches to over 5 feet, and there are frequent outcrops.

Oil shales have also been discovered in many other localities, including a promising shale field recently investigated near Baerami in the County of Hunter.

At Newnes 170,000 tons of torbanite were retorted in 1938 with yields up to 100 gal of oil per ton. A bench of 108 modified Pumpherston retorts at Glen Davis produced about 2½ million gal of petrol in 1945. It is estimated that this year, 1947, about 10 million gal of motor fuel will be produced from this field.

In 1938 the total reserves of New South Wales were estimated at 40 million tons of oil shale, but a more recent estimate, 1946, indicates that the shale reserves of Australia as a whole are comparatively small.

Tasmania. The only important deposit of oil shale in Tasmania is that found in the Coal Measures in the Mersey Valley, near Latrobe, known as "Tasmanite." The seam is about 5·2 inches thick and yields up to 18 gal of oil per ton. Although it is of the same geological age as that found in New South Wales it is inferior and differs considerably.

From 1930 to 1934, 14,600 tons of this shale were mined, producing 261,000 gal of crude asphaltic oil, the yield averaging 18 gal per ton.

The oil has a very objectionable smell due to the high percentage of sulphur and basic nitrogen compound which it contains.

As regards the reserves of oil shale in Tasmania, the latest estimate available, 1932, gave 31 million tons for the Latrobe and Oonah districts together.

New Zealand. Deposits of oil shale have been discovered in different parts of New Zealand. One of the most important was found at Orepuki, and an attempt was made to distil this shale in Pumpherston retorts which were installed there in 1900. In 1901 some 12,000 tons of shale were mined for oil production in these retorts, but the plant was closed down shortly afterwards because of the low grade of the shale and poor quality of the oil, which had a high sulphur content.

Canada.

Occurrences of oil shale deposits have been reported from each of the Canadian Provinces, notably at Collingwood, Ontario; Rosevale, New Brunswick; and in the Pictou County in the Province of Nova Scotia. The deposits of New Brunswick form a part of the Albert formation, which is the lowest known horizon of the Carboniferous System in that Province, and is correlated with the Carboniferous Calciferous Sandstone Series, which contains the oil shales of Mid- and West-Lothian in Scotland. The

oil shales of Nova Scotia are also associated with the Carboniferous. Some of the largest deposits are of poor quality.

The most important Canadian oil shale occurs in New Brunswick and is known as " Stellerite." The seams vary in thickness from 1 inch to 8 feet with oil yields averaging about 46 gal per ton. Rosevale shale averages 36 gal.

The Minister of Mines reported to the Canadian House of Commons, after a survey of the oil shales in 1943, that the best area of New Brunswick contained only 2 million tons of 20-gal shale associated with much lower grade material, confirming the conclusion that these deposits do not warrant further development.

South Africa.

In South Africa vast oil shale deposits occur (including Triassic, Carboniferous, and Permian), in particular in Natal at Impendhle and Utrecht, and in the Transvaal at Mooifontein and Bloemfontein. The field extends for about 250 miles from Ermelo in the Transvaal to Impendhle in Natal with frequent outcrops, the seams being under 2 feet thick with an average oil yield of 40 gal per ton. The shale reserves were estimated by G. A. Troye in 1946 to be 25 million tons. Yields up to 106 gal of oil have been reported.

The Ermelo deposits have been developed since 1910 with large-scale plants which produced in 1940 more than 3 million gal of shale oil.

India and Burma.

Up to 1922 the only oil shales known in the Indian Empire were those found east of the Amherst district, Burma. These are abundant and of Tertiary age. Tests made on bulk samples in Pumpherston retorts in 1926 gave 35 gal of oil and 40 lb of ammonium sulphate per ton.

These oil shales of Southern Burma, probably of Pliocene age, are remarkably persistent along the prospected belt of the Mepale Basin.

Since that date oil shale has also been discovered in similar Tertiary formations in the Shan States of Burma, and thin beds of Cambrian age in the Punjab. The outcrops in Burma are difficult to locate because of the dense jungle.

Brazil.

The main deposits of oil shale in Brazil occur near the Inferno River in the region of Codó.

The oil shales found on the coast of Alagôas belong to the Eocene age, and yield from 26 to 38 gal of oil per ton.

The best quality Marahú shale is said to belong to the Carboniferous and Tertiary, and is known as " Marahuito," yielding up to 100 gal of oil per ton.

Large deposits of a similar shale have also been found near the Jucú Valley, and in several other localities.

The " Olyoca " deposits, south of the Jucú Valley, gave an average yield of about 100 gal of oil which, at the last International Congress on

[*By courtesy U.S. Bureau of Mines.*

THE PLANT AREA AT RIFLE, COLORADO, FROM THE SOUTH, SHOWING RETORTS, CRUSHING PLANT, AND AUXILIARY BUILDINGS.

[*To face p.* 124.

[*By courtesy U.S. Bureau of Mines.*

THE N-T-U OIL-SHALE PROCESSING PLANT AT RIFLE, COLORADO, SHOWING CONVEYORS, STORAGE BINS, CRUSHING PLANT, AND, IN THE BACKGROUND, THE SHALE CLIFFS.

Carbonization Processes held in Philadelphia 10 years ago, was stated to be the richest in oil content of the world's known bituminous shale. It also has a large wax content of about 40 per cent, similar to Montan wax.

A shale plant was in operation in 1943 near Sao Paulo for the production of oil from local bituminous shales, and diesel engine trains on the Central Brazilian Railways ran satisfactorily on the oil obtained from this source.

United States of America.

Oil shales occur in many parts of the United States and belong to several different geological groups and formations. The richest oil shales are found in the Rocky Mountain region in the Green River formation of Eocene age.

The shales of Nevada are possibly slightly younger than the Green River, but most of those of Montana are older and belong to the Upper Paleozoic. The black shales of the Eastern States found in Illinois, Missouri, Indiana, New York, Kentucky, Ohio, Pennsylvania, and Tennessee, occur mainly in the Upper Devonian, but extensive deposits have also been found in the Lower Devonian and Ordovician.

The shales of California belong to the Miocene, but with few exceptions these deposits are not true oil shale. Before the discovery of petroleum in Pennsylvania, which practically put an end to shale retorting in the U.S.A, there were about sixty plants in the United States distilling oil from shales and cannel coal. The locations of these plants are known and a study of the local shales shows that they only yielded from 8 to 20 gal of oil per ton.

Soon after the First World War, a joint investigation was undertaken by the State of Colorado and the U.S. Bureau of Mines, with the primary object of finding the most favourable conditions of retorting Colorado oil shales to get the maximum yield of oil, which amounts to 60 U.S. gal per ton.

Since 1926 the Bureau of Mines have investigated different processes for extracting oil from oil shale.

A modern Scottish plant did not give the best results with Colorado shales, because the retorting of the latter is more difficult owing to it swelling on heating.

The fact that petroleum and its products were so plentiful, cheap, and easily obtained in the United States has ruled out hitherto any commercial large-scale production of oil from the vast resources of oil shales, which have been known to exist for many years in the States of Utah, Colorado, Wyoming, Nevada, California, and elsewhere in the West. There was no inducement for private enterprise, or for the State, to launch a shale oil industry and market substitutes for petroleum, whilst the cost of production could show no reasonable profits.

The latest estimate of the American workable oil shale deposits of the Tertiary oil shales of the Rocky Mountain States, the Devonian black shales of the Central States, and the cannel shales of the Central Eastern States is 400,000 million tons, and represents a recoverable production of about 92,000 million brl of crude oil, or enough to supply the needs of the United States for at least 65 years.

No further interest was taken in the exploitation and possible commercial utilization of these shales until the passing of the Synthetic Liquid Fuels

TABLE I.

Compiled from Published data by Technical Information Division, Anglo-Iranian Oil Co. Ltd.

State.	Geology.	Seam Thickness.	Yield per Ton Shale		Characteristics.	Reserves.	Nitrogen content, per cent.
			Oil, gal.	$(NH_4)_2SO_4$ lb.			
California	—	Very thick.	20	—	Soft, brownish, smells strongly of petroleum when freshly broken.	—	—
Colorado (N.W.)	Green River Formation. Tertiary	Rich oil shale strata from few inches up to 30 feet.	35–60	20	Colour varies from grey to brown, more massive shales dark brown to black.	Payable shale for many years.	—
Wyoming (S.W.)	Green Fiver Formation.	20–49 feet	35–60	20	—	—	—
Utah (N.E.)	Green River Formation (Largest deposits).	20–49 feet	35–60	20	—	—	—
Nevada	Deposits lie in big shallow basins.	4 feet	28	—	Lighter coloured than Green River Formation Shales for same yield of oil.	—	0·43
Montana	Phosphoria Formation of Permian strata.	—	20	7000	High percentage of phosphates. Dark brown to black, weathered surface bluish-white. Smell of petroleum when freshly broken. Readily combustible. Phosphorus 2% calculated at P_2O_5.		
	Tertiary beds interstratified with sandstones and lignite.	5 feet	24	—	Light brown, nearly white on weathered surfaces.	—	0·9
Kentucky and Eastern States	Mainly Upper Devonian. Also Lower Devonian Ordovician and Carboniferous.	—	16	58·6	Black or brown. High percentage of sulphur.	Very large but of poor quality.	—

Act, S.1243, by Congress in 1945, two divisions of which are concerned with the exploitation and utilization of oil shale.

Attention was again focused on the problem of being prepared to utilize other sources of hydrocarbon oils than natural petroleum, in view of the rapidly increasing post-war demands for motor fuel, and the possible exhaustion of the petroleum reserves in the United States. Although it did not appear economical to exploit the large-scale production of shale oil immediately, the Act made it clear that it was highly desirable for national security and future self-sufficiency to continue the researches which had already begun, with a view to finding the best method of obtaining the oil from shale, and to develop any likely process on a demonstration plant to full-scale commercial operation. For this purpose the Bureau of Mines concentrated on the operation of a new oil shale Research Station and Development Laboratory at the University of Wyoming, Laramie, and on the operation of a demonstration plant to mine and process about 200 tons of oil shale per day, yielding from 7,000 to 10,000 imp. gal of shale oil daily.

This 200 brl of crude shale oil per day capacity demonstration plant installed by the U.S. Bureau of Mines at Rifle, Colo., in the heart of the Rocky Mountain shale beds, was put on stream with elaborate dedication ceremonies on May 17, 1947. It is intended to construct a full-scale commercial retorting plant later, based on the demonstration plant, to produce at least 350,000 imp. gal of shale oil per day.

The work now in progress at the demonstration plant and laboratories in Colorado and Wyoming includes a complete study of the physical characteristics and chemical composition of oil-shales from the different States, and of the oil derived from them, and also the processing of these materials to yield marketable oil products as economically as possible, with a view to large-scale production in the future, if need be.

Table I summarizes the oil shales which have been so far located in the U.S.A., based on the information available at present. The major part and the richest deposits so far located are in the States of Colorado, Wyoming, and Utah. It will be noted that there are many gaps in the table.

In addition to the shale deposits mentioned in the Table attention has also been paid to those in Indiana and Ohio and other Eastern States to establish the economic value of these deposits, but so far their yield appears to be low compared with the Western shales.

There are, however, a number of favourable factors to offset this, particularly that many thousands of acres of these deposits can be mined cheaply by steam-shovels, and the fact that both the quantity and quality of the motor fuel obtainable from these shales is higher than that produced from many Western shales.

The latest known method of distilling shale continuously is one patented recently by the Standard Oil Development Co. (No. 586,992, April 10, 1947).

It makes use of the " fluidized " solid mass principle employed in the well-known fluid catalytic cracking process of the petroleum industry. The solids are sufficiently finely divided to cause them, when suspended in a gas or vapour, to flow through the distillation and regeneration zones of the plant in a form closely resembling that of liquid.

The fluid catalyst type of operation is at present being used, or has been

proposed for application, in many chemical and petroleum catalytic conversion processes where continuous, rather than intermittent, operation is desired. Up to date the most extensive application has been in the petroleum industry, where fluid catalytic cracking is now a well-established process and standard practice in many oil refineries.

When this principle is adapted to the treatment of shale the distillation is effected by contact of recycled superheated spent shale with preheated raw shale whilst both are in a "fluidized" and extremely turbulent condition. This process may prove to be particularly valuable in localities where petroleum is not available. It requires little or no extraneous heat for the retorting of the shale. This process has already been tried out successfully in the U.S.A. on a 1-ton per day plant, and a 100-ton per day plant will be in operation by the end of this year.

Conclusions.

The rate of consumption curve of liquid fuels from petroleum is continually rising from year to year, and will undoubtedly jump up steeply as soon as petrol rationing, shortage of materials, and the present-day depression ends. Fortunately, oil shale is widely distributed throughout the world and represents a potential source of fuel and power of considerable magnitude. Besides natural gas it is, in fact, one of the few naturally occurring sources of oil which, with few exceptions, has so far hardly been exploited for oil production. As a result of recent fluid catalytic developments it is stated that motor spirit can be produced now from natural gas and soon from coal in the U.S.A. as cheaply as from petroleum.

In this paper attention has been called to the value of shale oil as a means of contributing to the ever-increasing world demands for liquid fuels. It is a subject of international importance, because the world's limited supplies of coal and oil are inevitably shrinking fast.

This survey has shown clearly the urgent need for a more systematic study of the world's oil shales and their utilization to the best advantage. Much remains to be done, not only by geologists, but also by industrial and research chemists.

From the very incomplete data on oil shale reserves at present available, it has been found that more than 1 million million tons of oil shale have already been proved, but as the estimates published so far only apply to a few of the many countries in which oil shale deposits have been located, this figure represents a part only of the world's aggregate stock of oil shale which will ultimately be found to exist.

The object of this paper has been threefold :—

(1) To sound a note of warning on the inevitable exhaustion, or inaccessibility to the world's markets at some future date, of the world's coal, petroleum, and natural gas supplies as sources of fuel and power;

(2) To direct attention to the large potential reserves of the world's oil shale deposits, the exploitation and utilization of which have, with few exceptions, so far received comparatively little commercial development. A fuller investigation of these reserves is called for in view of

the fact that shale oil is one of the most readily available substitutes for petroleum in countries where oil shale occurs. It is by no means the most expensive alternative, although at present the only substitute likely to compete economically with petroleum is synthetic oil from natural gas;

(3) To emphasize the importance of the recent discovery of uranium as a by-product of oil shale, and the possible use of shale uranium as a source of atomic energy by fission.

Long before all the world's natural gas and the available oil shale has been used up for the production of oil, atomic power will have begun to take its place along with other forms of heat energy and power. There will certainly be no lack of raw material to supply all the uranium required.

It is now known that the rocks comprising the earth contain about four parts per million by weight of uranium, or about 800 times as much uranium as gold, and yet the extraction of gold is common practice! Amongst the rocks which have been proved to contain appreciable quantities of extractable uranium are certain oil shales and spent shales. To what extent this shale uranium can be made use of as a potential source of atomic energy is a problem for the chemists to solve.

In Sweden intensive research is now being carried out to find the best method of extracting uranium from oil shale. The Swedish Atomic Committee, composed of ten leading scientists, has already recommended the Swedish Government to form a company A.B.Atomenergi, with capital contributed jointly by the State and industry to design and build an experimental plant for the liberation of atomic energy using uranium from the oil shale deposits in the central Swedish provinces of Närke and Västergötland, and later to erect a plant for the production of atomic energy from this raw material on an industrial scale.

Acknowledgments.

The author desires to express his thanks to Dr G. M. Lees, chief geologist, Anglo-Iranian Oil Co. Ltd., to Dr G. H. Smith, chief chemist of Scottish Oils Ltd., and Dr Josef Eklund, of the Geological Survey of Sweden, for supplying some of the information included in this paper, and in particular to Mr F. P. Walton, technical information officer of the Anglo-Iranian Oil Co. Ltd., for his invaluable assistance in the preparation of the paper. The author is also indebted to Dr R. R. Sayers, director of the U.S. Bureau of Mines, for the photographs of the plant at Rifle, Colorado, and for permission to reproduce these. He wishes to thank Sir William Fraser, chairman of the Anglo-Iranian Oil Co. Ltd., for permission to publish this paper.

Appendix A.

World Production of Oil-Shale in Metric Tons.

(1 Metric Ton = 0·98421 English or Long Ton = 2204·6 lb).

	1922	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937
Australia (N.S.W.) .	*	*	*	352	2,165	2,734	*	203	*	*	*
Tasmania . .	*	2,637	4,368	5,515	1,425	1,115	3,456	3,329	37	*	*
Estonia . .	138	446,117	517,653	497,955	499,495	495,811	499,969	588,958	604,288	766,410	1,121,860
France . . .	61	77,047	78,606	82,500	78,350	91,400	91,000	102,340	88,473	*	*
Germany . .	*	670	603	544	418	401	553	869	722	874	*
Gt. Britain (Scotland)	2,620,455	2,070,826	2,056,088	2,052,939	1,760,557	1,390,562	1,419,410	1,423,257	1,430,976	1,432,036	*
Italy . . .	5	1,560	1,331	938	713	1,268	918	749	1,118	889	*
U.S.S.R. . .	18	562	*	*	*	318,200	201,600	206,400	417,000	700,000	*
Spain . . .	*	54,110	54,900	55,147	55,611	64,132	60,448	37,783	*	*	*
U.S. . . .	*	1,928	1,767	*	*	*	*	*	*	*	*
China (Manchuria) .	*	*	*	*	1,245,097	1,412,558	2,683,440	2,105,765	3,436,647	*	*
Yugoslavia . .	*	*	*	*	*	*	*	479	260	137	527

Compiled from Statistical Appendix to U.S.A. Minerals Year Book 1922–38. * = data not available.

APPENDIX B.

Average Chemical Composition, etc., of Some Typical Shales and Spent Shales.

	Scotland Dunnet Shale, West Lothian (*a*)	*France* St. Hilaire (*b*)	*Estonia* Kukersite (*c*)	*Sweden* Närke (*d*)	*Sweden* Oland (Alum Shale) (*d*)	*Germany* Württemberg (*e*)	*Australia* Capertee Valley (*f*)	*South Africa* (*g*)	*U.S.A.* Green River, Wyo. (*h*)
RAW SHALE.									
Oil Yield { Percentage	8·3	6·7	20·7	5·5	2·5	4·4	43·8	22·3	9·2
Oil Yield { Gal/ton	21	16·6	51·5 (25–78)	13	6·4	11·3	112	57·7	23·45
Gas per ton shale, cu. ft.	—	880	—	—	—	2024	3045	2230	—
Total ash in shale, %	73·26	—	32	73	82	80·5	29·15	35·6	64·8
Total sulphur in shale, %	1·27	1·2	—	6·8	2·5	As / FeS_2 7	0·516	—	3·84
COMPOSITION OF ASH:									
SiO_2	49·58	45·7	28·8	—	—	40·0	29·6	—	41·9
CaO	5·60	14·0	42·9	—	—	29·0	1·4	—	17·6
Al_2O_3	27·98	21·3	7·2	—	—	14·6	64·4	—	18·8
Fe_2O_3	8·96	10·5	6·8	—	—	6·8	3·05	—	
MgO	2·19	2·5	1·8	—	—	2·0	0·3	—	10·9
SO_3	3·77	3·0	—	—	—	4·8	—	—	—
Other alkalis and undetermined	1·92	3·0	Na_2O / K_2O 3·6	—	—	2·2	—	—	—

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APPENDIX C.

Uranium Content in a Swedish Oil-Shale Deposit (Norrtorp).

Depth, metres.	Percentage uranium in shale.	Percentage uranium in ash.
6·1–7·2	0·009	0·012
7·2–8·4	0·014	0·018
8·7–9·8	0·018	0·024
10·0–11·2	0·027	0·037
11·2–12·6	0·022	0·030
12·6–14·0	0·015	0·021
14·4–16·2	0·010	0·014
16·7–18·1	0·010	0·015
18·1–19·5	0·009	0·012
19·5–21·0	0·005	0·007
21·8–22·3	0·003	0·004

From information given privately to the author for inclusion in this paper, by Dr Josef Eklund, Geologist, Geological Survey of Sweden, May 20, 1947.

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THE ALKYLATION OF *ISO*PARAFFINS WITH OLEFINS IN THE PRESENCE OF SULPHURIC ACID. PART II. THE ACTION OF SULPHURIC ACID ON THE TRIMETHYLPENTANES.

By Frank Morton (Fellow) and Alan R. Richards (Fellow).

Summary.

The action of sulphuric acid upon various trimethylpentanes has been studied and it is shown that using 98·5 per cent acid at 10° C the order in which the trimethylpentanes react is 2 : 3 : 4-trimethylpentane > 2 : 2 : 4-trimethylpentane > 2 : 2 : 3-trimethylpentane. The main reaction is a disproportionation accompanied by isomerization. The rate of isomerization is slow and cannot be regarded as a major reaction in the alkylation of *iso*paraffins with olefins.

Introduction.

Isomerization of the product of reaction between *iso*paraffins and olefins in the presence of aluminium chloride [14] and sulphuric acid [2,3] has been suggested as a possible explanation of the nature of the final products isolated as a result of these reactions. Owing to the difficulty of analysis of mixtures of paraffins, isomerization of the octanes has not been extensively studied. Birch, Dunstan [2] *et al* have shown that various trimethylpentanes when stirred with 97 per cent sulphuric acid at ordinary temperatures are converted into mixtures of hydrocarbons. These studies indicated that whilst 2 : 2 : 4-, 2 : 2 : 3-, and 2 : 3 : 4-trimethylpentanes, 2 : 2 : 5-trimethylhexane and 2 : 3-dimethylbutane were attacked by sulphuric acid, resulting in a complex mixture of hydrocarbons, *iso*pentane, 2 : 2-dimethylbutane, and 2 : 2 : 3-trimethylbutane were not attacked. McAllister [19] *et al* have reported that the primary effect of sulphuric acid upon the trimethylpentanes is a cleavage into C_4 fragments, resulting in the formation of *iso*butane and high molecular weight polymers. These authors therefore considered that rearrangement of the trimethylpentanes was not responsible for the complex nature of the alkylate. The conditions used by McAllister *et al* are not given, but it is suggested that 100 per cent acid and room temperature (?25° C) were used.

More recently, Ciapetta [6] has suggested a carbonium ion mechanism to account for the complex nature of the products of the alkylation reaction in which the first formed carbonium ion undergoes rearrangement in accordance with the postulates of the Whitmore theory.[26] The reaction of *iso*butane with butenes leads, according to this mechanism, to the formation of the carbonium ion of 2 : 2 : 3-trimethylpentane which according to Ciapetta undergoes rearrangement to give ultimately a mixture of 2 : 2 : 4-, 2 : 2 : 3-, 2 : 3 : 4-, and 2 : 3 : 3-trimethylpentanes. Since 2 : 2 : 3-trimethylpentane is found in alkylate only in relatively small amounts,[6] the carbonium ion postulated by Ciapetta must be the least stable of the trimethylpentane ions. This is contrary to the findings of Birch and Dunstan *et al*.[2]

A study of the effect of sulphuric acid upon the trimethylpentanes alone, in mixtures, and in the presence of various added substances, has therefore been undertaken. As a preliminary the effect of sulphuric acid of different concentrations upon 2 : 2 : 4-trimethylpentane was studied at 30° C and at 10° C. Using 100 per cent sulphuric acid at 30° C the main reaction was one of cleavage to C_4 fragments. *iso*Butane was formed in considerable quantity and the acid layer became increasingly dark. At the end of the experiment a considerable amount of unsaturated material could be recovered by dilution of the acid. Using 97 per cent sulphuric acid at 10° C, however, the reaction was entirely different. No detectable quantity of *iso*butane was formed and the acid layer remained clear. Upon dilution of the acid only traces of unsaturated hydrocarbons were detected.

The reaction was then investigated in greater detail, under conditions which approximate to those prevailing in an alkylation unit. The investigation was confined to one acid strength (98·5 per cent H_2SO_4) one hydrocarbon/acid ratio, one temperature (10° C $\pm$ 0·5° C), and within experimental limits the degree of agitation was constant. The contact time and the nature of the trimethylpentane were the only variables.

Experimental.

Materials Used.

Sulphuric Acid.—Pure sulphuric acid was redistilled *in vitro*. The resulting colourless product was adjusted by the addition of distilled water to a final strength of 98·5 per cent H_2SO_4 by weight. The acid was analysed by breaking a weighed glass ampoule, containing about 1 gram of acid, under the surface of 250 ml of ice-cold distilled water and titrating with N/2NaOH.

n-*Pentane* and iso*Pentane*.—These two hydrocarbons were obtained in a substantially pure state by two refractionations of commercial samples (from gasoline light fractions) on small (1 foot by 1 inch) Stedman packed columns.

n-*Butyl Alcohol*.—Baker's C.P. grade was used as supplied.

2 : 2 : 4-*Trimethylpentane*.—This material was isolated from an aviation alkylate by repeated fractionation (cf Part I: *J. Inst. Petrol.*, 1947, 33, 697) and was over 99·5 per cent pure. The physical constants are given in Table I.

Table I.

Refractive Index (n_D^{20}) *of Trimethylpentanes.*

Hydrocarbon.	n_D^{20}.		Probable purity, mol %.
	Found.	Literature.	
2 : 2 : 4-Trimethylpentane . .	1·3870	1·3868	>99·0
2 : 2 : 3-Trimethylpentane . .	1·3980	1·3980	>99·5
2 : 3 : 4-Trimethylpentane . .	1·4000	1·3997	88
2 : 3 : 3-Trimethylpentane . .	1·4007	1·4028	30

2 : 2 : 3-*Trimethylpentane*.—This material was obtained by repeated fractionation of the suitable fraction of "*iso*octane" produced by U.O.P.

phosphoric acid polymerization of *iso*butylene followed by hydrogenation. Spectroscopic analysis of the material showed it to be over 99 per cent 2 : 2 : 3-trimethylpentane (cf Table I for physical constants).

2 : 3 : 4-*Trimethylpentane*.—This material was also obtained by refractionation of "*iso*octane." It contained some 2 : 3 : 3-trimethylpentane, probably not more than 10 per cent.

2 : 3 : 3-*Trimethylpentane*.—Pure 2 : 3 : 3-trimethylpentane was not available. In order to obtain some information as to the behaviour of this compound a fraction obtained during the analysis of commercial alkylate (cf Part I) containing 30 per cent 2 : 3 : 3-trimethylpentane and 70 per cent 2 : 3 : 4-trimethylpentane was used.

Apparatus.

The apparatus (Fig. 1) consisted of a 2-litre, 3-neck flask fitted with a thermometer and mercury-seal stirrer. The stirrer was similar to an ordinary T-type stirrer except that the stirring arm was made from tubing with the ends drawn out to form jets and a hole in the centre. The contents

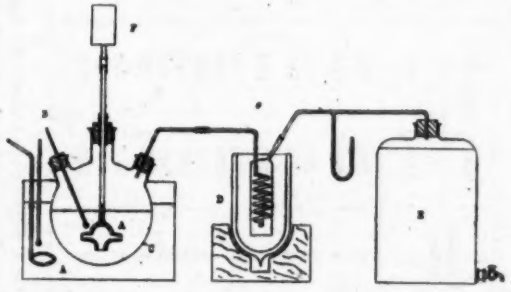


FIG. 1.

A. Stirrers.
B. Thermometers.
C. 2-Litre flask.
D. Dewar flask.
E. 5-Litre aspirator.
F. Electric motor—Palo-Myers constant speed.

of the flask were therefore sucked in through the centre hole and forced out through the jets by centrifugal force. The stirrer was driven by a "Palo-Myers" constant speed motor and the stirring was efficient and reproducible.

The outlet from the flask was connected via a trap cooled in solid CO_2/gasoline to a manometer and aspirator. The experiments were conducted at atmospheric pressure and the gas collected over water. The reaction flask was immersed in a bath and the temperature of the reactants maintained at $10 \pm 0{\cdot}5°$ C at all times throughout the experiments.

At the completion of the experiment the contents of the flask were separated and the oil layer washed with sodium carbonate solution, twice with ice-cold water, and dried over anhydrous sodium sulphate. The products were then fractionated, using columns packed with 4 feet of ⅛-inch Stedman packing operated at a nominal reflux ratio of 119 : 1. From the physical constants of the resulting fractions it was possible to make an estimate of their composition. The details of the various

TABLE II.

Isomerization of isoOctanes in 200 ml of 98·5% H_2SO_4 at 10° C.

Run no.	Charge.	Vol, ml.	Contact time, hr.	Volume (ml.) after		Vol of gas, ml.	Reaction loss allowing for gas (*a*), ml.	Washing loss (*b*), ml.	Transfer loss (*c*), ml.	Vol charged to still, ml.
				Acid.	Oil.					
4	2 : 2 : 4-Trimethylpentane	200	4	205	185	1550	4	5	15	165
5	2 : 2 : 4-Trimethylpentane *iso*Pentane	200 110	4	208	283	760	16	5	28	250
6	Alkylate bottoms	200	4	205	190	300	3	3	—	148
7	2 : 3 : 4-Trimethylpentane	200	4	208	188	950	—	8	5	175
8	2 : 2 : 4-Trimethylpentane Normal pentane	200 110	4	200	293	200	16	6	12	275
9	2 : 3 : 4-Trimethylpentane	200	2	200	190	1100	5	7	13	170
10	2 : 3 : 4-Trimethylpentane	200	1	200	190	1000	4	6	7	177
11	2 : 2 : 4-Trimethylpentane	200	2	200	185	1000	11	5	10	170
12	2 : 3 : 3-Trimethylpentane	200	2	207	180	1100	7 (*d*)	6	2	172
13	2 : 2 : 3-Trimethylpentane	200	2	200	189	100	10½	9	10	170
14	2 : 2 : 4-Trimethylpentane	200	1	202	188	430	8	8	—	180
15	2 : 2 : 4-Trimethylpentane *n*-Butyl alcohol	207 30	2	212	206	900	13	1	5	200
16	2 : 2 : 3-Trimethylpentane *n*-Butyl alcohol	202 30	2	225	200	120	6	—	5	195

Notes on losses :—All losses are on a volume basis. On a weight basis some of the figures would be increased—others decreased.
(*a*) Total volume, oil, and acid, charged to reactor less total volume recovered less equivalent liquid vol of gas distributed equally.
(*b*) 3 ml distributed equally—remainder *pro rata* between C_5 and dimethylbutanes.
(*c*) Loss due to storage, bottling, and still charging. 3 ml assumed C_5 + dimethylbutanes. Remainder distributed equally.
(*d*) 1 ml of light distillate in CO_2 trap.

TABLE III.

TABLE III.

Isomerization of isoOctanes. Analysis of Isomates.

All volumes in ml.

Constituents.	Cut pts, °C.	Run. No.												
		4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
*iso*Pentane	40	19	49	—	25	35† 34*	15†	30†	30	29	5	10†	23	3
2 : 3-Dimethylbutane	72	5	9	—	7	5	3	8	4	5½	—	4	2	—
2 : 4-Dimethylpentane + 2 : 3-Dimethylpentane	96	9	3	—	9	4	8	10	5	11½	1	5	6	—
2 : 2 : 4-Trimethylpentane	103	46	109	—	23	118	23	20	90	16	1	129	105	1
2 : 4-Dimethylhexane + 2 : 5-Dimethylhexane	110	9	7	—	16	1	13	(12)‡	7	16	—	2	6	—
2 : 2 : 3-Trimethylpentane	110	—	—	—	—	—	—	—	—	—	142	—	—	170
2 : 3 : 4-Trimethylpentane + 2 : 3 : 3-Trimethylpentane	116	10	12	—	25	8	35	(58)‡	12	41	—	—	7	—
2 : 3-Dimethylhexane + 3 : 4-Dimethylhexane	121	5	2	—	4	1	4	3	1	3	—	—	7	—
2 : 2 : 5-Trimethylhexane	128	7	15	2	18	10	16	9	1	15½	—	—	7	—
2 : 3 : 5-Trimethylhexane	146	8	—	1	7	—	7	—	—	6½	—	—	7§	—
Remainder + residue		38	20	145	39	24	33	25	15	23	17	25	28	22
Loss		9	24	—	2	35	13	2	5	5	4	5	2	Gain 1
Charge		165	250	148	175	275	170	177	170	172	170	180	200	195

* *n*-Pentane.
† Some *n*-pentane.
‡ Plateau at 146° C not included.
§ Split not definite due to bad still operation.

experiments are given in Table II, whilst the results of the fractionation of the products are recorded in Table III. In view of the small quantity of gas produced in these experiments no analyses were undertaken.

Results.

Considerable difficulty has been experienced in establishing a basis whereby the results could be compared because of the unavoidable loss of pentanes during the washing operations. The losses have been carefully apportioned and the data of Table III re-written in Table IV as a percentage of the effective volume of the sample. Details of the losses are given in footnotes to Table II. The relative values in each analysis given in Table IV of the material boiling above *iso*pentane are reliable, but when comparisons are made between one analysis and the next, the error in the *iso*pentanen-pentane content must be taken into account.

2 : 2 : 4-*Trimethylpentane*.—Experiments 4, 11, and 14 show the effect of increased reaction time upon the decomposition of 2 : 2 : 4-trimethylpentane. It will be seen from Fig. 2 that the rate of decomposition decreases slowly with increasing time of reaction and after 4 hours the reaction does not appear to have reached equilibrium conditions. The initial reaction appears to result in the formation of *iso*pentane, some C_9 hydrocarbons, and higher boiling material. Continued reaction results in the formation of small amounts of C_6, C_7, and C_9 hydrocarbons together with some isomeric octanes and a marked increase in the amount of high boiling material. The C_5, C_8, and C_7 material increases only slowly after 2 hours reaction.

Experiments 5 and 8 show the effect of added *iso*- and *n*-pentanes on this reaction. It is clear that the nature of the pentane has little effect. In both cases the result has been to depress the rate of decomposition of the 2 : 2 : 4-trimethylpentane into higher boiling material. It is noteworthy that the isomerization seems to be suppressed to a lesser extent than the other reactions. The effect is probably merely that of an inert diluent and similar effects have been observed in the operation of alkylation units as a result of increasing the amount of *n*-butane in the feed. In effect, the inert diluent reduces the acid–*iso*paraffin interface and thus reduces the reaction rate. In the alkylation reaction the presence of an inert diluent reduces the *iso*paraffin–acid olefin interface and in effect is equivalent to decreasing the *iso*paraffin–olefin ratio.

The effect of addition of olefin to the reaction was studied in Experiment 15. *n*-Butyl alcohol was added in a quantity sufficient to react with 100 per cent sulphuric to produce 98·5 per cent sulphuric acid and *n*-butene (presumably present as the carbonium ion). The reaction products contained slightly less pentane and somewhat more C_9 and higher boiling material, but the extent of isomerization of the 2 : 2 : 4-trimethylpentane was unaltered.

2 : 3 : 4-*Trimethylpentane and* 2 : 3 : 3-*Trimethylpentane*.—As would be expected from the presence of three tertiary carbon atoms, 2 : 3 : 4-trimethylpentane reacts much more rapidly than 2 : 2 : 4-trimethylpentane. The decomposition does not follow a unimolecular law. This may be accounted for by the fact that the material was contaminated with a slower

TABLE IV.

Isomerization of iso*Octanes.*

Corrected Analyses in Percent of Isomate.

Run no.	4.	11.	14.	7.	9.	10.	12.	13.	4.	5.	8.	11.	15.
Contact time, hr.	4.	2.	1.	4.	2.	1.	2.	2.	4.	4.	4.	2.	2.
Charge	2:2:4-trimethylpentane.	2:2:4-trimethylpentane.	2:2:4-trimethylpentane.	2:3:4-trimethylpentane.	2:3:4-trimethylpentane.	2:3:4-trimethylpentane.	2:3:3-trimethylpentane.	2:2:3-trimethylpentane.	2:2:4-trimethylpentane.	2:2:4-trimethylpentane + isopentane.	2:2:4-trimethylpentane + n-pentane.	2:2:4-trimethylpentane.	2:2:4-trimethylpentane + n-butyl alcohol.
Loss + pentanes (mainly iso)	19	23	11	18	14	20	22	10	19	30	39	25	13
2:3-Dimethylbutane	4	2	3	5	2	5	3½	—	4	3	2	2	1
2:4- and 2:3-Dimethylpentane	5	3	3	5	4½	5½	6	½	5	1	1½	3	3
2:2:4-Trimethylpentane	26½	51½	69	12	13	11	9	½	26½	43	42	51½	52
2:4- and 2:5-Dimethylhexane	5	4	1	9	7½	(6½)	9	—	5	3	½	4	3
2:2:3-Trimethylpentane	—	—	—	—	—	—	—	79½	—	—	—	—	—
2:3:4- and 2:3:3-Trimethylpentane	6	7	—	14	20	(32)	23	—	6	5	3	7	3½
2:3- and 3:4-Dimethylhexane	3	½	—	2	2	1½	2	—	3	1	½	½	3½
2:2:5-Trimethylhexane	4	½	—	10	9	5	9	—	4	6	3½	½	3½
2:3:5-Trimethylhexane	5	—	—	4	4	—	3½	—	5	—	—	—	3½
Remainder + residue	22½	8½	13	21	19	13½	13	9½*	22½	8	8	8½	14
Summary													
Below C_8	28	28	17	28	20½	30½	31½	10½	—	34	43½	28	17
Unchanged C_8	26½	51½	69	14	20	(32)	23	79½	—	43	42	51½	52
Isomers	14	11½	1	23	22½	19	20	10	—	9	4	11½	10
Above C_8	31½	9	13	35	32	18½	26½		—	14	11½	9	21

* I.B.P. 108° C.

reacting impurity (*i.e.*, 2 : 3 : 3-trimethylpentane). It is clear from Fig. 2 that the initial reaction is the most rapid encountered in this series of experiments. The reaction appears to have reached some measure of equilibrium after only 1 hour and subsequent reaction consists mainly in the formation of C_9 and higher boiling hydrocarbons (cf Experiments 7, 9, and 10). The extent of isomerization is greater than in the case of 2 : 2 : 4-trimethylpentane. Possibly the failure of the isomers to accumulate still further after the initial reaction is accounted for by their undergoing

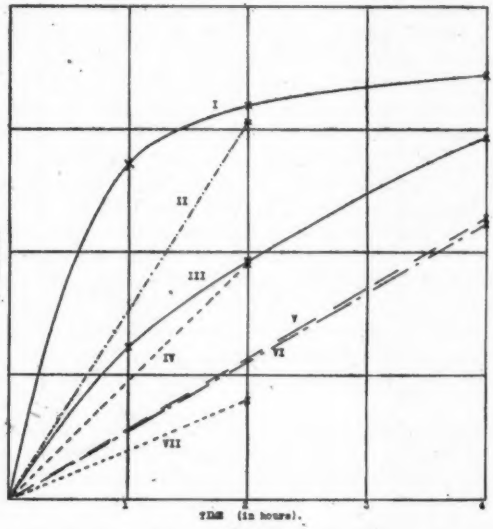


FIG. 2.

DECOMPOSITION OF TRIMETHYLPENTANES AT 10° C IN 98·5% H_2SO_4.

I. 2 : 3 : 4-Trimethylpentane.
II. 2 : 3 : 3-Trimethylpentane and 2 : 3 : 4-trimethylpentane.
III. 2 : 2 : 4-Trimethylpentane.
IV. 2 : 2 : 4-Trimethylpentane and *iso*butene.
V. 2 : 2 : 4-Trimethylpentane and *iso*pentane.
VI. 2 : 2 : 4-Trimethylpentane and *n*-pentane.
VII. 2 : 2 : 3-Trimethylpentane.

decomposition. The apparently large amount of 2 : 4-dimethylhexane (Table IV) may contain undetected 2 : 2 : 3-trimethylpentane.

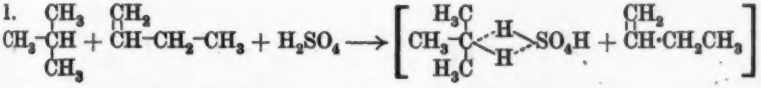
2 : 3 : 3-Trimethylpentane from the limited data available does not show any significant differences from 2 : 3 : 4-trimethylpentane. The reaction is apparently slower and less higher boiling material is formed as a result.

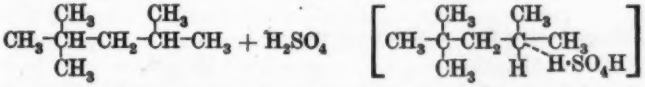
2 : 2 : 3-*Trimethylpentane.*—This trimethylpentane reacts much more slowly than any of the others. The formation of *iso*pentane is definite, but the nature of the higher boiling material could not be determined on the quantity available. The presence of *iso*butene did not result in any increase of reaction rate. There was very little, if any, isomerization.

Discussion.

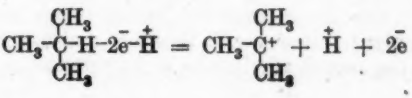
Despite the uncertainty introduced by the losses of light hydrocarbons, the results show that the order in which the trimethylpentanes react with 98·5 per cent sulphuric acid is 2 : 3 : 4-trimethylpentane > 2 : 2 : 4-trimethylpentane > 2 : 2 : 3-trimethylpentane. The initial reaction appears in all cases to involve a breakdown into *iso*pentane accompanied by the formation of nonanes and higher boiling paraffins. Subsequently a certain amount of isomerization takes place, but only in the case of 2 : 3 : 4-trimethylpentane can this be regarded as a major reaction. The isomerization is accompanied by the formation of hexanes, heptanes, and nonanes, the major constituents of these fractions being 2 : 3-dimethylbutane, 2 : 4- and 2 : 5-dimethylpentanes, 2 : 2 : 5-trimethylhexane accompanied by traces of the monomethylpentanes and hexanes. The isomerization of the trimethylpentanes is not accelerated by the addition of olefin, as might be expected to be the case if the reaction followed the mechanism suggested by Schmerling,[22,23] the only observable effect of the addition of *n*-butene being the formation of high boiling material by the alkylation of the *iso*paraffin. The addition of *iso*pentane has little effect on the course of the reaction, *n*-pentane behaving in a precisely similar manner and exerting a slight suppressive effect similar to that observed on the addition of inert diluents in the alkylation reaction.

The formation of *iso*pentane from 2 : 2 : 4- or 2 : 2 : 3-trimethylpentane involves a double C–C cleavage. In view of the slow rate of isomerization and of the appearance of hydrocarbons containing six, seven, and nine carbon atoms it appears unlikely that the reaction proceeds via the formation of the trimethylpentane carbonium ion. Moreover, the rate of decomposition and isomerization of the trimethylpentanes is not sufficiently rapid to justify the assumption that the observed products of the alkylation reaction are produced by subsequent breakdown of a trimethylpentane. It seems more reasonable to assume that the products obtained in the alkylation of *iso*butane by butenes are formed by the breakdown of a hydrocarbon–sulphuric acid complex, a similar complex being formed more slowly by the action of sulphuric acid upon the trimethylpentanes.

1. 

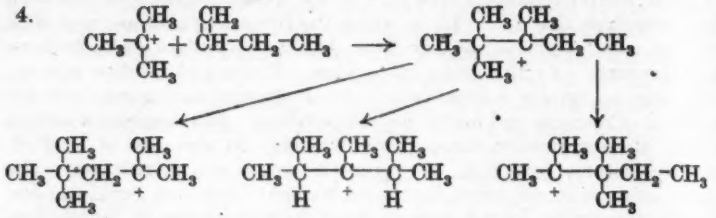
2. 

It has been suggested [6] that in the alkylation of *iso*paraffins by olefins in the presence of sulphuric acid a carbonium ion is formed by loss of proton and electrons from the *iso*paraffin.

3. 

This carbonium ion then reacts with the olefin to give a carbonium ion which undergoes rearrangement as follows :—

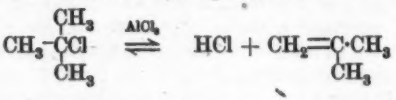
4.



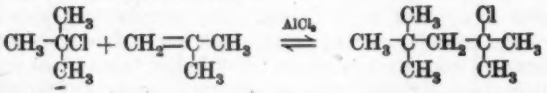
Subsequent addition of proton and electrons giving the observed mixture of trimethylpentanes.

A somewhat similat mechanism has been proposed by Schmerling [22] for the alkylation of *iso*paraffins by olefins in the presence of aluminium chloride in which the olefin is considered to initiate a chain reaction summarized as follows :

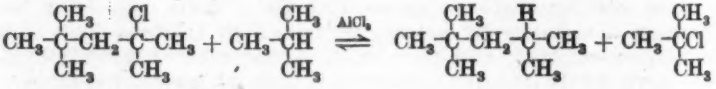
5. Reversible elimination of hydrogen halide :—



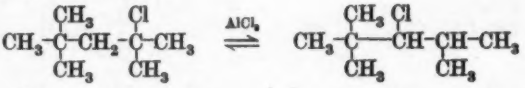
6. Addition of halide to alkene :—



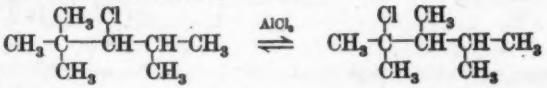
7. Halogen–hydrogen exchange :—



8. Partial isomerization :—



9. Wagner–Meerwein rearrangement :—

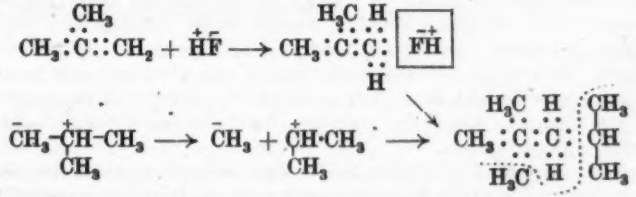


This mechanism overcomes many of the difficulties inherent in the mechanism proposed by Ciapetta, and subsequent work by Schmerling [23] and by Bartlett [1] has shown that the various steps proposed can be experimentally realized. However, it does not satisfactorily explain the observed facts in the case of alkylations in the presence of sulphuric acid.

According to this mechanism the isomerization of the trimethylpentanes should proceed via the intermediate formation of a trimethylpentane sulphate (or halide in the presence of $AlCl_3$) and yield products comparable with those obtained by alkylation of *iso*butane with butenes in the same media whilst the isomerization should be facilitated by the presence of an olefin. The present work shows that using sulphuric acid this is not the case and that the isomerization of the trimethylpentanes cannot be assumed to be a major step in the overall alkylation mechanism.

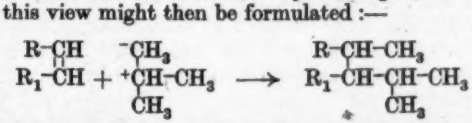
More recently a mechanism has been proposed by Gorin, Kuhn, and Miles [11] in which the primary products of the reaction are assumed to be formed by " a two-step mechanism in which (1) the olefin reacts with the catalyst to form an addition complex via co-ordination with two electrons from the double bond, and (2) the addition product reacts with *iso*butane to produce the final product and release the catalyst. In step (2) the *iso*butane molecule is assumed to behave as if it becomes polarized into a negative methyl fragment and a positive *iso*propyl fragment as it approaches the olefin catalyst complex."

10.



Isomeric products are assumed to be produced by hydride shifts in the olefin–catalyst complex prior to reaction with the *iso*paraffin. The assumption that carbon–carbon cleavage occurs in the *iso*paraffin molecule was made both by McAllister *et al* [19] and by Caesar and Francis.[5] McAllister showed that the presence of a tertiary carbon atom in the reacting *iso*paraffin was an essential condition of the reaction and assumed that cleavage of the *iso*paraffin was due in some way to the action of sulphuric acid at the tertiary carbon atom. Gorin *et al* regard the tertiary carbon of the *iso*paraffin as relatively electropositive, because the hydrogen attached thereto undergoes exchange reactions with alkyl halides,[1] and since in this reaction it replaces a negative chlorine atom, the hydrogen itself must be negatively charged in the presence of the catalyst. This view is similar to that held by Degering [7] who regards the activity of the tertiary hydrogen in *iso*butane as due to the displacement of the electrons away from the tertiary carbon atom. By this concept the carbon atoms of the three methyl groups in *iso*butane are relatively electronegative whilst the tertiary carbon atom itself is relatively electropositive. The reaction according to this view might then be formulated :—

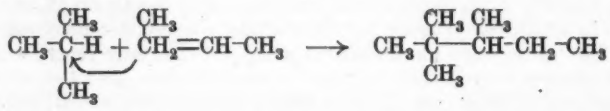
11.



the function of the catalyst being to facilitate polarization of the *iso*paraffin

and to increase the activity of the olefin by formation of catalyst–olefin complex.

The mechanism proposed by Gorin *et al* not only accounts for the formation of the *iso*paraffins found in the various alkylation reactions studied, but it also accounts for the non-appearance of 2 : 2 : 3-trimethylpentane, which by the classical mechanism originally proposed by Ipatieff and Grosse [15] should be the principal product of the reaction between *iso*butane and butene-2 :—

12. 

Although the higher *iso*paraffins undergo disproportionation and carbon–carbon cleavage there is little evidence that *iso*butane itself is either isomerized or broken down by treatment with sulphuric acid (both isomerization and disproportionation occur with aluminium halides [20, 25] etc). Under the conditions of the alkylation reaction *iso*butane can be circulated with sulphuric acid for several hours without any apparent change. It would therefore appear that the presence of the olefin is necessary before the *iso*butane can react and that the carbon–carbon cleavage postulated by McAllister *et al* and by Gorin *et al* does not occur until the attack by the olefin upon the *iso*paraffin has succeeded—at least in part.

Both Gorin and McAllister consider that isomerization of the olefin is responsible for the production of several products from one *iso*paraffin and one olefin, and other workers have assumed that secondary reactions of the olefin (polymerization, depolymerization, hydrogenation, etc) contribute largely to the complexity of the products.[8] In certain instances hydrogenation of the olefin has been established,[16] but in general adequate proof of the reactions ascribed to the olefin is lacking. Whilst it is true that the use of a more reactive olefin (*iso*butene) in the alkylation of *iso*butane leads to a more complex product than is obtained by the use of butene-1 or butene-2, it is unlikely that this is a result of action between the olefin and sulphuric acid alone. The alkylation of benzene with *iso*butene using 98 per cent sulphuric acid as catalyst produces only *tert.*-butylbenzene.[14] Further alkylation using excess *iso*butene leads to the production of *p*-di-*tert.*-butylbenzene. The alkylation of benzene with chlor*iso*butene gives a 68 per cent yield of α-chloro-β-phenyl-*iso*-butane [27] accompanied by *p*-di-(β-chloro-*tert.*-butyl) benzene.[24] The alkylation of toluene by styrene in 98 per cent sulphuric acid [18] and the formation of 1 : 1-diphenylethane by the action of acetylene on benzene in sulphuric acid [21] further illustrate the fact that in 98 per cent sulphuric acid the most reactive olefins enter directly into alkylation reactions and do not undergo the polymerization and other reactions so characteristic of olefins in acid of lower concentration. Hammett [12] has interpreted these facts to imply that in 98 per cent sulphuric acid the olefins are converted into the carbonium ion with such rapidity that the polymerization reaction which requires the presence of the olefin and the carbonium ion, is unable to compete with the alkylation reaction.

The alkylation of methyl*cyclo*hexane with *n*-butenes in sulphuric acid media yields a product of constant boiling point [19] (by comparison with the products obtained using aluminium chloride this is probably a mixture of 1 : 3- and 1 : 4-methylbutyl*cyclo*hexanes). The alkylation of methyl-*cyclo*pentane by *n*-butenes yields a mixture of 1 : 3-dimethyl-5-ethyl- and 1 : 3-dimethyl-4-ethyl-*cyclo*hexane unaccompanied by *iso*pentane or the isomeric hexanes, heptanes, and octanes so characteristic of the reaction of *iso*paraffins with the same olefins.[16] It would therefore appear that the formation of complex products in the alkylation of *iso*paraffins is due largely to the tendency of the *iso*paraffin to undergo carbon–carbon cleavage, and that this cleavage in certain instances can be brought about by the action of sulphuric acid alone.

Conclusions.

From the foregoing discussion, it will be realized that none of the proposed mechanisms is entirely satisfactory and there is insufficient evidence available in support of any single reaction mechanism. The present state of our knowledge may be summarized as follows :—

The isoparaffin *reacts by virtue of a reaction centre at the tertiary carbon atom. It is probable that the initial reaction involves proton exchange with the catalyst,*[13] *and this may either increase the polarity of the adjacent carbon–carbon linkage or it may increase the electron availability at this point thus rendering attack by the olefin more easy of accomplishment. It is also highly probable that the action of the acid catalyst orientates the* isobutane *molecule at the acid–hydrocarbon interface.*

There is some question as to the mechanism by which the olefin reacts, but there is a considerable body of evidence to indicate that it reacts as a carbonium ion formed by the addition of proton from the catalyst. If this is the case, then obviously the mechanism proposed by Schmerling, which involves the formation of a carbonium ion from the isoparaffin *cannot be correct.*

The possibility of hydride shifts in the olefin itself has been proposed by various workers, but in the foregoing discussion it has been shown that the experimental evidence available does not support this view, and in the authors' opinion alkylation by olefins in 98 *per cent sulphuric acid is not accompanied by olefin isomerization to any marked degree.*

Isomerization of the final product cannot be a major cause of the complexity of the reaction products since this reaction is far slower than would be required to account for the observed products under normal conditions.

It is obvious that further experimental work is necessary before the complex mechanism of the alkylation reaction can be clearly understood, and for the moment it would appear that the most satisfactory explanation of this reaction is that which involves the intermediate formation of an *iso*paraffin–olefin–catalyst complex [9, 10] which by some mechanism, involving intra- and inter-molecular migration of methyl groups produced by cleavage of carbon–carbon bonds in the *iso*paraffin fragment leads to the complex reaction products observed.

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